# Influence of the Halogen in Titanocene Halide Promoted Reductions

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 $Ti^{III}$  species generated in tetrahydrofuran by a Zn-based reduction of  $Cp_2TiX_2$  (X = Cl, Br, and I) have been identified by means of cyclic voltammetry and kinetic measurements to be a mixture of  $Cp_2TiX$ ,  $(Cp_2TiX)_2$ , and  $Cp_2Ti^+$ . The distribution of these species is found to be dependent on the halogen in that  $Cp_2Ti^+$  is formed in quite substantial amounts for X = Brand I, but not at all for X = Cl. In all three solutions  $Cp_2TiX$  and  $(Cp_2TiX)_2$  are present in appreciable amounts characterized by a dimerization equilibrium constant of  $(1-3) \times 10^3 \text{ M}^{-1}$ . The reactivity of  $(\text{Cp}_2\text{TiX})_2$  is larger than or comparable to that of  $\text{Cp}_2\text{TiX}$ and Cp<sub>2</sub>Ti<sup>+</sup>, as assessed in their reactions with benzyl chloride and benzaldehyde. In addition, the rate data are essentially independent of the halogen, and no correlation is observed with the standard potentials determined in cyclic voltammetry for the different Ti<sup>IV</sup>/Ti<sup>III</sup>based redox pairs. This indicates high inner-sphere character of the electron transfer processes. Analysis of the diastereoselectivities found for the hydrobenzoin formation in the titanocene chloride promoted pinacol couplings of benzaldehyde shows high *dl:meso* ratios of 97:3 with a decreasing trend as X is changed from Cl to Br and I. This effect is suggested to be due to stereoelectronic interactions between the titanocene moieties in the developing Ti<sup>IV</sup>-bound pinacolate of the transition state.

# Introduction

In recent years, metal-reduced titanocene dichloride,  $Met-Cp_2TiCl_2$  (Met = Zn, Mn, and Al), has found interesting applications as selective single-electrondonating reagents, where stoichiometric amounts of the metal are employed to generate Ti<sup>III</sup>-based species from reduction of Cp<sub>2</sub>TiCl<sub>2</sub>.<sup>1</sup> Such reagents have found widespread use in synthetic organic chemistry, promoting highly diastereoselective pinacol coupling reactions,<sup>2</sup> epoxide openings to alkyl radicals,<sup>3</sup> reductions of alkyl halides such as glycosyl bromides<sup>4</sup> and vic-dibromides,<sup>5</sup> Reformatsky additions,<sup>6</sup> and others.<sup>7–9</sup> Furthermore, interesting catalytic versions of some of the synthetic transformations have been developed, whereby Ti<sup>III</sup> is regenerated in situ after electron transfer to the substrate.<sup>1</sup> Despite their importance, information concerning the nature and reactivity of the Ti<sup>III</sup> species formed in Met-Cp<sub>2</sub>TiCl<sub>2</sub> solutions has been lacking. Such information is undoubtedly crucial for the application of these reducing agents to other transformations, as well as for the design of asymmetric variants of the above reactions.<sup>1</sup>

Recently, we have elucidated the mechanism of the electrochemical and metal-induced reductions of Cp<sub>2</sub>-TiCl<sub>2</sub> in tetrahydrofuran (THF) by means of cyclic voltammetric and kinetic measurements.<sup>10</sup> We were able to demonstrate that the principal constituents of the Met-Cp<sub>2</sub>TiCl<sub>2</sub> solutions were the monomeric Cp<sub>2</sub>TiCl and dimeric (Cp<sub>2</sub>TiCl)<sub>2</sub>.<sup>10</sup> Trinuclear complexes or ionic clusters were not the reacting species in solution<sup>11</sup> despite their isolation and characterization in the solid phase.<sup>12</sup> In Chart 1, we have collected the proposed structures of Cp<sub>2</sub>TiX (I), (Cp<sub>2</sub>TiX)<sub>2</sub> (II and III), and the trinuclear complex (IV) using X as a symbol for the halogen and assuming that any free coordination site will be occupied by a solvent molecule, i.e., THF. The symmetric arrangement II of the dimer is based on an analysis of the solid-state structure,<sup>13</sup> and it is not known to what extent this structure in solution can be partly broken to the half-open arrangement III as discussed elsewhere.<sup>10c</sup>

One of the questions that came out of our previous studies is related to the importance of the chlorine in Met-Cp<sub>2</sub>TiCl<sub>2</sub> and whether this halogen can be substituted with bromine or iodine. So far Met-Cp<sub>2</sub>TiBr<sub>2</sub> and Met-Cp<sub>2</sub>TiI<sub>2</sub> have not found the same extensive use as reductants as Met-Cp<sub>2</sub>TiCl<sub>2</sub>. Accordingly, one of the aims of the present paper is to investigate the prospects in using such systems with particular emphasis addressed at clarifying the identity of the species present, their reactivities, and the influence exerted by the

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Chart 1. Proposed Structures of Cp<sub>2</sub>TiX (I), (Cp<sub>2</sub>TiX)<sub>2</sub> (II and III), and Trinuclear Complexes (IV) in THF



halogen on the diastereoselectivity for the hydrobenzoin formation in pinacol coupling reactions involving benzaldehyde. A detailed mechanistic investigation of the electrochemical behavior of Zn-Cp<sub>2</sub>TiBr<sub>2</sub> and Zn-Cp<sub>2</sub>TiI<sub>2</sub> is carried out in order to examine whether they can be encompassed in the same scheme as outlined previously for Zn-Cp<sub>2</sub>TiCl<sub>2</sub>.<sup>10c</sup> The electron-donating properties of the different Ti<sup>III</sup>-based species identified are elucidated in their reactions with benzyl chloride and benzaldehyde. Finally, our study will allow us to propose how stereoelectronic effects may play an important role in controlling the diastereoselective outcome of the Met-Cp<sub>2</sub>TiX<sub>2</sub>-promoted pinacol coupling.

## **Results and Discussion**

Our previous cyclic voltammetric studies of Met- $Cp_2$ -Ti $Cl_2$  in THF gave immediate access to a characteriza-

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tion of the redox processes shown in eqs 1-4 pertaining to the four  $Ti^{III}$ -based species  $Cp_2TiCl_2^-$ ,  $(Cp_2TiCl)_2$ ,  $Cp_2$ -TiCl, and  $Cp_2Ti^+.^{10}$ 

$$\operatorname{Cp}_{2}\operatorname{TiX}_{2}^{-} - e \rightleftharpoons \operatorname{Cp}_{2}\operatorname{TiX}_{2}$$
 (1)

$$(Cp_2TiX)_2 - e \rightleftharpoons (Cp_2TiX)_2^+$$
(2)

$$Cp_2TiX - e \rightleftharpoons Cp_2TiX^+$$
 (3)

$$Cp_2Ti^+ - e \rightleftharpoons Cp_2Ti^{2+}$$
 (4)

A detailed analysis of the electrochemical behavior revealed that only  $Cp_2TiCl$  and  $(Cp_2TiCl)_2$  were actual constituents in the solutions, whereas the other species were formed as the result of follow-up reactions occurring during the cyclic voltammetric sweep. It was also suggested that  $Cp_2TiCl$  is generated in either of the metal-induced reductions depicted in eqs 5–7, while the presence of  $(Cp_2TiCl)_2$  is due to the reversible dimerization reaction depicted in eq 8, independent of the metal.

$$\operatorname{Zn} + 2\operatorname{Cp}_2\operatorname{TiX}_2 \rightarrow \operatorname{ZnX}_2 + 2\operatorname{Cp}_2\operatorname{TiX}$$
 (5)

$$Mn + 2Cp_2TiX_2 \rightarrow MnX_2 + 2Cp_2TiX$$
 (6)

$$Al + 3Cp_2TiX_2 \rightarrow AlX_3 + 3Cp_2TiX$$
(7)

$$2Cp_2TiX \stackrel{k_8}{\underset{k_{-8}}{\longleftrightarrow}} (Cp_2TiX)_2$$
(8)

In the present work cyclic voltammograms of Zn-Cp<sub>2</sub>-TiBr<sub>2</sub> and Zn-Cp<sub>2</sub>TiI<sub>2</sub> were recorded to elucidate if the mechanistic picture would be the same as for Zn-Cp<sub>2</sub>-TiCl<sub>2</sub>. A selection of voltammograms for all three kinds of solutions is collected in Figures 1 and 2. In our previous detailed analysis of Zn- $Cp_2TiCl_2$  it was shown that the first broad oxidation wave appearing at ca. -0.8 V vs Fc<sup>+</sup>/Fc (abbreviation for ferrocenium/ ferrocene) splits into two waves upon increasing the sweep rate, encompassing the oxidation of both (Cp<sub>2</sub>- $TiCl)_2$  in eq 2 and  $Cp_2TiCl$  in eq 3, i.e., the two constituents in the equilibrium reaction of eq 8.<sup>10c</sup> These electrode processes are followed by chemical reactions, where Cp<sub>2</sub>Ti<sup>+</sup> with the characteristic oxidation wave at -0.4 V vs Fc<sup>+</sup>/Fc corresponding to eq 4 is generated either from a so-called father-son reaction involving Cp<sub>2</sub>-TiCl and  $Cp_2TiCl^+$  or from a direct fragmentation of  $(Cp_2TiCl)_2^+$  as shown in eqs 9 and 10, respectively.

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**Figure 1.** Cyclic voltammograms of 2 mM Zn-Cp<sub>2</sub>TiCl<sub>2</sub> (-),<sup>10c</sup> 2.2 mM Zn-Cp<sub>2</sub>TiBr<sub>2</sub>  $(\cdot \cdot \cdot)$ , and 2.2 mM Zn-Cp<sub>2</sub>TiI<sub>2</sub>  $(- - \cdot)$  recorded at a sweep rate of 0.1 V s<sup>-1</sup> in 0.2 M Bu<sub>4</sub>-NPF<sub>6</sub>/THF. Currents are normalized with respect to sweep rate.



**Figure 2.** Cyclic voltammograms of 2 mM Zn-Cp<sub>2</sub>TiCl<sub>2</sub> (-),<sup>10c</sup> 2.2 mM Zn-Cp<sub>2</sub>TiBr<sub>2</sub>  $(\cdot \cdot \cdot)$ , and 2.2 mM Zn-Cp<sub>2</sub>TiI<sub>2</sub>  $(- - \cdot)$  recorded at a sweep rate of 10 V s<sup>-1</sup> in 0.2 M Bu<sub>4</sub>-NPF<sub>6</sub>/THF. Currents are normalized with respect to sweep rate.

$$Cp_{2}TiX + Cp_{2}TiX^{+} \underbrace{\stackrel{k_{9}}{\longleftarrow}}_{k_{-9}} Cp_{2}Ti^{+} + Cp_{2}TiX_{2} \quad (9)$$

$$(\mathrm{Cp}_{2}\mathrm{TiX})_{2}^{+} \underbrace{\stackrel{k_{10}}{\longleftrightarrow}}_{k_{-10}} \mathrm{Cp}_{2}\mathrm{Ti}^{+} + \mathrm{Cp}_{2}\mathrm{TiX}_{2} \qquad (10)$$

The major peak present on the reverse sweep at ca. -1.2 V vs Fc<sup>+</sup>/Fc originates from the reduction of Cp<sub>2</sub>-TiCl<sub>2</sub> (see eq 1) produced in the two above reactions. Thus, one of the main conclusions from these studies is that Cp<sub>2</sub>Ti<sup>+</sup> and Cp<sub>2</sub>TiCl<sub>2</sub> in contrast to Cp<sub>2</sub>TiCl and (Cp<sub>2</sub>TiCl)<sub>2</sub> are not present initially in the Zn-Cp<sub>2</sub>TiCl<sub>2</sub> solution.

The voltammograms pertaining to Zn-Cp<sub>2</sub>TiBr<sub>2</sub> and Zn-Cp<sub>2</sub>TiI<sub>2</sub> show clear resemblances to those of Zn-Cp<sub>2</sub>-TiCl<sub>2</sub>. First of all, the peak at ca. -0.4 V vs Fc<sup>+</sup>/Fc coincides in all cases, independent of X, which proves that the generation of Cp<sub>2</sub>Ti<sup>+</sup> is a general feature of these systems. For the broad oxidation wave appearing in the range from -0.8 to -0.5 V vs Fc<sup>+</sup>/Fc, on the other hand, there is a distinct dependence on the nature of X. In analogy with the interpretation of the Zn-Cp<sub>2</sub>TiCl<sub>2</sub> case, this feature is attributed to the presence of two



**Figure 3.** Cyclic voltammograms of 2.2 mM solutions of Zn-Cp<sub>2</sub>TiBr<sub>2</sub> (-), Mn-Cp<sub>2</sub>TiBr<sub>2</sub> (· · ·), and Al-Cp<sub>2</sub>TiBr<sub>2</sub> (- -) recorded at a sweep rate of 1.0 V s<sup>-1</sup> in 0.2 M Bu<sub>4</sub>-NPF<sub>6</sub>/THF. Inset: Cyclic voltammogram of 2 mM Cp<sub>2</sub>TiBr<sub>2</sub> recorded at a sweep rate of 1.0 V s<sup>-1</sup> in 0.2 M Bu<sub>4</sub>NPF<sub>6</sub>/THF.

electrode processes with the first wave (appearing at the most negative potential) assigned to the oxidation of (Cp<sub>2</sub>TiX)<sub>2</sub> and the second one to the oxidation of Cp<sub>2</sub>-TiX. The presence of the dimerization equilibrium reaction involving these two species in eq 8 is revealed by the fact that the ratio of the currents for the first and second peak increases with a lowering of the sweep rate (compare Figures 1 and 2) and/or an increase of the concentration. Because of the dynamic nature of the cyclic voltammetric technique and the fact that the dimer is easier to oxidize than the monomer, it is possible to let most of the oxidation process go through the dimer at low sweep rate. Upon increasing the sweep rate, it becomes harder for the equilibrium reaction to keep up, and accordingly much more of the oxidation will go through the monomer. In that instance, the electrochemical response provides a better picture of the actual composition of the solution. As it was the case for Zn-Cp<sub>2</sub>TiCl<sub>2</sub>, the wave of Cp<sub>2</sub>Ti<sup>+</sup> decreases relative to the wave(s) of (Cp<sub>2</sub>TiX)<sub>2</sub> and Cp<sub>2</sub>TiX as the sweep rate is increased and/or the concentration is lowered. This supports the interpretation that Cp<sub>2</sub>Ti<sup>+</sup> is generated during the sweep because of the follow-up reactions occurring in eqs 9 and 10. However, a closer examination of the peak current ratios reveals that this tendency is less pronounced for X = Br and I than Cl, providing a first indication that there are differences in the equilibrium distribution of the Ti<sup>III</sup>-based species for different X.

To reveal if the metal employed in the reduction of  $Cp_2TiX_2$  should have any influence on the composition of the solutions, cyclic voltammograms of  $Zn-Cp_2TiX_2$ ,  $Mn-Cp_2TiX_2$ ,  $Al-Cp_2TiX_2$ , and  $Cp_2TiX_2$  (X = Br and I) were recorded as shown in Figures 3 and 4. As seen, the oxidation peak potentials attributed to  $(Cp_2TiX)_2$  and  $Cp_2TiX$  are independent of the metal, which indicate that trinuclear complexes involving a central metal atom are not present in either of these solutions (see IV in Chart 1). For  $Al-Cp_2TiBr_2$  and  $Al-Cp_2TiI_2$  an additional peak is apparent at ca. -1.0 and -0.9 V vs  $Fc^+/Fc$ , respectively, which we assign to the oxidation of  $Cp_2TiBr_2^-$  and  $Cp_2TiI_2^-$ , respectively, consistent with the cyclic voltammograms recorded of authentic samples



**Figure 4.** Cyclic voltammograms of 2.2 mM solutions of Zn-Cp<sub>2</sub>TiI<sub>2</sub> (-), Mn-Cp<sub>2</sub>TiI<sub>2</sub> (· · ·), and Al-Cp<sub>2</sub>TiI<sub>2</sub> (- -) recorded at a sweep rate of 1.0 V s<sup>-1</sup> in 0.2 M Bu<sub>4</sub>NPF<sub>6</sub>/THF. Inset: Cyclic voltammogram of 2 mM Cp<sub>2</sub>TiI<sub>2</sub> recorded at a sweep rate of 1.0 V s<sup>-1</sup> in 0.2 M Bu<sub>4</sub>NPF<sub>6</sub>/THF.

of Cp<sub>2</sub>TiBr<sub>2</sub> and Cp<sub>2</sub>TiI<sub>2</sub> (see insets of Figures 3 and 4). Exactly the same phenomenon was observed for a solution of Al-Cp<sub>2</sub>TiCl<sub>2</sub>, in which an oxidation wave pertaining to Cp<sub>2</sub>TiCl<sub>2</sub><sup>-</sup> was detectable, although to a smaller extent.<sup>10c</sup> The broad oxidation wave appearing on the reverse sweep in the voltammogram of Cp<sub>2</sub>TiI<sub>2</sub> encompasses both the oxidation of Cp<sub>2</sub>TiI<sub>2</sub><sup>-</sup> and the Cp<sub>2</sub>TiI/(Cp<sub>2</sub>TiI)<sub>2</sub> system formed upon fragmentation of iodide from Cp<sub>2</sub>TiI<sub>2</sub><sup>-</sup> as reported elsewhere.<sup>10b</sup> Even in the voltammogram of Cp<sub>2</sub>TiBr<sub>2</sub> small oxidation waves of Cp<sub>2</sub>TiBr/(Cp<sub>2</sub>TiBr)<sub>2</sub> are detectable on the reverse sweep along with the distinct Cp<sub>2</sub>TiBr<sub>2</sub><sup>-</sup> peak; these waves become more pronounced upon increasing the sweep rate.<sup>10b</sup>

The influence of the metal halides formed in eqs 5-7pertains mainly to their involvement in halide transfer reactions. The halide abstraction proceeds with greater ease from aluminum halides compared to zinc and manganese halides, since the peak originating from the oxidation of Cp<sub>2</sub>TiX<sub>2</sub><sup>-</sup> can only be observed in the former case. This observation is surprising, as aluminum halides are the stronger Lewis acids, although it is not known to what extent a coordination between the metal halides and THF may affect the reactivities. At the same time the presence of these chemical reactions explains why the peaks of the Cp<sub>2</sub>TiX<sub>2</sub>/Cp<sub>2</sub>TiX<sub>2</sub><sup>-</sup> redox couple for the different Met-Cp<sub>2</sub>TiX<sub>2</sub> solutions are not completely coincident with those observed for  $Cp_2TiX_2$  and why there is a variation in the relative currents of the oxidation waves. The transformation of any of the (Cp<sub>2</sub>- $TiX)_2$ ,  $Cp_2TiX$ , and  $Cp_2Ti^+$  species into  $Cp_2TiX_2^-$  in cyclic voltammetry is facilitated by the presence of X<sup>-</sup>. For instance, addition of tetrabutylammonium iodide to a Zn-Cp<sub>2</sub>TiI<sub>2</sub> solution makes the voltammogram resemble that recorded for a sample of Cp<sub>2</sub>TiI<sub>2</sub> (see the Supporting Information). This does not mean that Cp<sub>2</sub>TiI<sub>2</sub><sup>-</sup> actually is present in the Zn-Cp<sub>2</sub>TiI<sub>2</sub> solution but rather that it is formed at the electrode surface during the sweep.<sup>10b</sup>

On the basis of the apparent mechanistic similarities for the electrochemical behavior of the different Met- $Cp_2TiX_2$  solutions, we propose that a common reaction

scheme, a so-called mesh scheme, can be set up as shown in Scheme 1.<sup>10c,14</sup> In the Supporting Information, detailed versions of this scheme are provided for Zn-Cp<sub>2</sub>TiBr<sub>2</sub> and Zn-Cp<sub>2</sub>TiI<sub>2</sub>. The mesh scheme incorporates the four relevant electrochemical processes, eqs 1-4, along with a number of chemical reactions, including eqs 8–10. In particular, the equilibrium reactions involving Cp<sub>2</sub>TiX<sub>2</sub><sup>-</sup>, Cp<sub>2</sub>TiX, (Cp<sub>2</sub>TiX)<sub>2</sub>, and Cp<sub>2</sub>Ti<sup>+</sup> are important, as they determine the actual composition of the solution, while the associated rate constants are essential parameters for describing the compositional changes occurring at the electrode surface during a sweep. The oxidation of both Cp<sub>2</sub>TiX and (Cp<sub>2</sub>TiX)<sub>2</sub> leads ultimately to the formation of Cp<sub>2</sub>Ti<sup>+</sup> and Cp<sub>2</sub>TiX<sub>2</sub> because Cp<sub>2</sub>TiX<sup>+</sup> reacts rapidly with Cp<sub>2</sub>TiX or with metal halides and  $(Cp_2TiX)_2^+$  fragmentates. However, at high sweep rates peaks corresponding to the reduction of  $Cp_2TiX^+$  and  $(Cp_2TiX)_2^+$  can be monitored in the cyclic voltammograms. Likewise, the absence at low sweep rates of a cyclic voltammetric reduction wave pertaining to Cp<sub>2</sub>Ti<sup>2+</sup> formed upon oxidation of Cp<sub>2</sub>Ti<sup>+</sup> in eq 4 suggests that Cp<sub>2</sub>Ti<sup>2+</sup> will abstract halides from the metal halides to afford  $Cp_2TiX_2$ . The lack of the  $Cp_2TiX_2^-$  oxidation wave in double sweep experiments for Met = Zn and Mn indicates that the halide transfer reactions may go the other way around also; that is, the metal halides can abstract a halide effectively from Cp<sub>2</sub>TiX<sub>2</sub><sup>-</sup> produced upon the electrochemical reduction of Cp<sub>2</sub>TiX<sub>2</sub> in eq 1. In general, Ti<sup>IV</sup>- but not Ti<sup>III</sup>-based species thus are capable of abstracting halides from the metal halides with the Al-Cp<sub>2</sub>TiX<sub>2</sub> system presenting a notable exception, as the Cp<sub>2</sub>TiX<sub>2</sub><sup>-</sup> wave in this case is observable.

In the further analysis of the cyclic voltammograms the goal was to obtain quantitative information about the composition of the solutions. The focus was mainly on Zn-Cp2TiBr2 and Zn-Cp2TiI2, since the voltammograms in these cases were the ones being least influenced by halide transfer reactions. This simplifies the mechanistic scheme and makes the analysis less uncertain. In general, all relevant potentials, heterogeneous and homogeneous rate constants, and equilibrium constants have been extracted by digital simulations of the experimentally obtained voltammograms recorded at different sweep rates of 0.1–50 V s<sup>-1</sup> and concentrations of 1.0–2.2 mM. All simulations and fittings were carried out using the program DigiSim 3.03.<sup>15</sup> For such measurements, it is important that the number of experimental observations is large to diminish the overall uncertainty. In addition, the whole collection of voltammograms recorded for each solution has been simulated simultaneously to obtain the most consistent set of results. A complete and detailed description of the exact model parameters used, a discussion of the uncertainties associated with the procedure, as well as relevant fits can be found in the Supporting Information.

<sup>(14)</sup> Usually the presence of at least three redox states as well as chemical states would be required for describing such a mechanism by a mesh scheme. Thus, in the present case one might argue that the mechanistic scheme is of the ladder type, if the  $(Cp_2TiX)_2^+$  species with its combination of  $Ti^{III}$  and  $Ti^{IV}$  atoms is not considered as representing a distinct redox state (see also: Evans, D. H. *Chem. Rev.* **1990**, *90*, 739).

<sup>(15)</sup> Rudolph, M.; Feldberg, S. W. *DigiSim version 3.03*; Bioanalytical Systems, Inc.: West Lafayette, IN.





Table 1. Relevant Data Extracted from Cyclic Voltammograms Recorded on Zn-Cp<sub>2</sub>TiX<sub>2</sub> Solutions<sup>a</sup>

	$\operatorname{Zn-Cp_2TiCl_2}{}^b$	$\operatorname{Zn-Cp_2TiBr_2}$	$ m Zn-Cp_2TiI_2$
$E_1^{\circ}/\mathrm{V} ~\mathrm{vs}~\mathrm{Fc/Fc}^{+\ c}$	$-1.20\pm0.03$	$-1.10\pm0.05$	$-0.95\pm0.05$
$E_2^{ m o}/{ m V}~{ m vs}~{ m Fc}/{ m Fc}^+$ $^c$	$-0.81\pm0.03$	$-0.76\pm0.05$	$-0.75\pm0.05$
$E_3^{\circ}$ /V vs Fc/Fc <sup>+ <math>c</math></sup>	$-0.75\pm0.03$	$-0.69\pm0.05$	$-0.67\pm0.05$
$E_4^{\circ}$ /V vs Fc/Fc <sup>+ c</sup>	$-0.43\pm0.03$	$-0.45\pm0.05$	$-0.43\pm0.05$
$k_{ m s,1}/ m cm~s^{-1}$	0.04	0.06	0.04
$k_{ m s,2}/ m cm~s^{-1}$	0.02	0.015	0.015
$k_{ m s,3}/ m cm~s^{-1}$	0.008	0.006	0.008
$k_{ m s,4}/ m cm~s^{-1}$	0.015	0.007	0.007
$K_8/{ m M}^{-1}$	$3~(2{-}5) imes~10^{3}$	$1~(0.5{-}3) imes 10^3$	$1~(0.5{-}3) imes10^{3}$
$k_{ m 8}/{ m M}^{-1}~{ m s}^{-1}$	$2(1{-}10) imes 10^4$	$2~(1{-}5) imes 10^{5}$	$5(2{-}10) imes10^5$
$k_{-8}/\mathrm{s}^{-1}$	6.7 (2-50)	$2~(1{-}5) imes 10^2$	$5(2{-}10) imes10^2$
$K_9 d$	$3.2 imes10^7$	$1.6 imes10^7$	$2.4 imes10^7$
$k_{ m 9}/{ m M}^{-1}~{ m s}^{-1}$	${}^{<}5 imes10^3$	$1~(0.5{-}2) imes 10^4$	$2(1{-}4) imes 10^3$
$k_{-9}/{ m M}^{-1}~{ m s}^{-1}$	$^{<}1.6 imes10^{-4}$	$6.3(3.2{-}13) imes10^{-4}$	$8.3~(4.2{-}17) imes10^{-5}$
$K_{10}/\mathrm{M}$	$1~(0.01{-}10^5) imes10^3$	$1~(0.01{-}10^5) imes10^3$	$1~(0.01{-}10^5) imes10^3$
$k_{10}/{ m s}^{-1}$	$3~(1{-}50) imes~10^2$	$3~(1{-}10^2) imes 10^2$	$3~(1{-}10^2) imes10^2$
$k_{-10}/{ m M}^{-1}~{ m s}^{-1}$	$0.3~(10^{-5} - 30)$	$0.3(10^{-6}{-}10)$	$0.3 \ (10^{-6} - 10)$

<sup>*a*</sup> The tabulated values are the ones providing the best fits, while those given in parentheses describe the intervals of tolerance, as determined from a manual adjustment of the parameters. To minimize the number of adjustable parameters, the uncertainties on the  $k_s$  values were not determined, but in general they can be assumed to be on the order of 50%. <sup>*b*</sup> From ref 10c. <sup>*c*</sup> Standard potentials are defined as reduction potentials and can be converted to SCE by adding 0.52 V. <sup>*d*</sup> Calculated automatically by the DigiSim program from a thermochemical cycle.

The essential data extracted from the simulation procedure are collected in Table 1 together with those obtained previously for X = Cl. A couple of points are worth noting. First of all, the agreement with the corresponding values obtained from the electrochemical reduction of Cp<sub>2</sub>TiX<sub>2</sub> is good.<sup>10b</sup> For a given X the order of standard potentials,  $E^{\circ}$ , for the four Ti-containing redox couples is as follows:  $Cp_2TiX_2/Cp_2TiX_2^- \ll (Cp_2-Cp_2TiX_2)^- (Cp_2-Cp_2TiX_$  $TiX)_2^+/(Cp_2TiX)_2 < Cp_2TiX^+/Cp_2TiX \ll Cp_2Ti^{2+}/Cp_2Ti^+;$ that is, from a thermodynamic point of view Cp<sub>2</sub>TiX<sub>2</sub><sup>-</sup> is expected to be a much stronger electron donor than Cp<sub>2</sub>Ti<sup>+</sup>. For a given Ti-based redox couple a relatively weak halogen effect is observed as  $E^{\circ}$  increases slightly in the order X = Cl, Br, and I; that is,  $Cp_2TiI$  would be expected on this basis to be a slightly weaker electron donor than Cp<sub>2</sub>TiCl. The halogen effect is largest for the Cp<sub>2</sub>TiX<sub>2</sub> series as the difference in standard potentials going from X = Cl to I constitutes 250 mV. In general, it may be concluded that the electronic influence on the titanium nucleus is smallest, when the ligand is the larger iodide than chloride.

The heterogeneous rate constants,  $k_s$ , associated with the four electrode processes are in the range 0.006–0.06 cm s<sup>-1</sup>. With respect to the equilibrium reaction in eq 8, relatively large differences are seen in the dimerization rate constant  $k_8$  as well as  $k_{-8}$ , although the equilibrium constant  $K_8$  is essentially independent of X:  $k_8 = 2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  for X = Cl,  $k_8 = 2 \times 10^5 \text{ M}^{-1}$ s<sup>-1</sup> for X = Br, and  $k_8 = 5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  for X = I. The large values of  $k_{-8}$  for X = Br and I are the origin of the significant appearance of Cp<sub>2</sub>TiX in the cyclic voltammograms of Zn-Cp<sub>2</sub>TiX<sub>2</sub> in these cases (see Figures 1 and 2). For the father-son reaction between Cp<sub>2</sub>TiX and Cp<sub>2</sub>TiX<sup>+</sup> in eq 9 and for the fragmentation reaction of (Cp<sub>2</sub>TiX)<sub>2</sub><sup>+</sup> in eq 10 the rate constants are found to be largely independent of X. On the other hand, the

Table 2. Equilibrium Concentrations of the Ti<sup>III</sup>-Based Species Present in 2 mM Solutions of Zn-Cp<sub>2</sub>TiX<sub>2</sub> and Electrochemically Reduced Cp<sub>2</sub>TiX<sub>2</sub><sup>*a*</sup>

		- <b>F</b> 22		
	$[Cp_2TiX_2^-]$	[Cp <sub>2</sub> TiX]	$[(Cp_2TiX)_2] \\$	$[Cp_2Ti^+]$
$\begin{array}{l} X = Cl \\ X = Br \\ X = I \end{array}$	$\begin{array}{c} 0.00 \ (1.35) \\ 0.00 \ (0.11) \\ 0.00 \ (0.02) \end{array}$	$\begin{array}{c} 0.50 \ (0.21) \\ 0.68 \ (0.39) \\ 0.60 \ (0.40) \end{array}$	$\begin{array}{c} 0.75 \ (0.22) \\ 0.47 \ (0.75) \\ 0.37 \ (0.79) \end{array}$	$\begin{array}{c} 0.00 \ (0.00) \\ 0.38 \ (0.00) \\ 0.66 \ (0.00) \end{array}$

 $^a$  Values for the electrochemically reduced solutions of  $\rm Cp_2TiX_2$  are given in parentheses, from ref 10b.

reactivity of  $Cp_2TiX^+$  and  $Cp_2Ti^{2+}$  toward the zinc halides decreases in the order X = Cl, Br, and I as envisioned by the pronounced presence of the reduction peaks of these two species in the voltammograms of Zn- $Cp_2TiBr_2$  and in particular Zn- $Cp_2TiI_2$  (see the Supporting Information).

On the basis of the equilibrium constants extracted for the different reactions involving Cp<sub>2</sub>TiX<sub>2</sub><sup>-</sup>, (Cp<sub>2</sub>TiX)<sub>2</sub>,  $Cp_2TiX$ , and  $Cp_2Ti^+$ , it is possible to determine the actual composition for any of the systems studied. In Table 2 the distribution is collected for 2 mM solutions of Zn-Cp<sub>2</sub>TiX<sub>2</sub> along with corresponding data evaluated for electrochemically reduced Cp<sub>2</sub>TiX<sub>2</sub>.<sup>10b</sup> The most interesting result provided by the new data pertaining to Zn-Cp<sub>2</sub>TiBr<sub>2</sub> and Zn-Cp<sub>2</sub>TiI<sub>2</sub> as compared with  $Zn-Cp_2TiCl_2$  is the existence of  $Cp_2Ti^+$  in substantial concentrations of 0.38 and 0.66 mM, respectively. The concentrations of Cp<sub>2</sub>TiX and (Cp<sub>2</sub>TiX)<sub>2</sub> are of the same magnitude, while there will be no Cp<sub>2</sub>TiX<sub>2</sub><sup>-</sup> at all, as  $X^-$  is bound in the metal halides.<sup>16</sup> To account for the presence of  $Cp_2Ti^+$  in the cases of X = Br and I, eq 5 has to be extended as shown in eq 11.

$$ZnX_2 + 2Cp_2TiX \rightleftharpoons ZnX_4^{2-} + 2Cp_2Ti^+ (X = Br \text{ and } I)$$
 (11)

The electrochemical reduction of  $Cp_2TiX_2$  is characterized by the absence of metal halides, and under these conditions an equilibrium mixture of  $Cp_2TiX$  and  $(Cp_2TiX)_2$  is formed for all X with no indication of  $Cp_2Ti^+$  as seen for Zn-Cp<sub>2</sub>TiBr<sub>2</sub> and Zn-Cp<sub>2</sub>TiI<sub>2</sub>. Moreover, for X = Cl the main constituent actually becomes  $Cp_2TiCl_2^-$  (see Table 2). Thus, it may be concluded that the presence of zinc halides in the Zn-Cp<sub>2</sub>TiX<sub>2</sub> solutions favors the generation of the more halogen-deficient Ti<sup>III</sup> species, and as the titanium-halogen bond becomes weaker in the order X = Cl, Br and I,<sup>17</sup> this trend is getting more pronounced.

#### **Kinetic Studies**

With the aim of describing the reactivity of the different  $Ti^{III}$ -based species, kinetic studies were carried out on reactions involving the two electron acceptors benzyl chloride, BnCl, and benzaldehyde, PhCHO. The kinetic situation is quite complex, as the Zn-Cp<sub>2</sub>TiX<sub>2</sub> solution consists of an equilibrium mixture of Cp<sub>2</sub>TiX,  $(Cp_2TiX)_2$ , and  $Cp_2Ti^+$  for X = Br and I as evaluated in Table 2. In our previous study concerning Zn-Cp<sub>2</sub>TiCl<sub>2</sub>, the task was simpler due to the absence of Cp<sub>2</sub>Ti<sup>+</sup>. In

that case the reactivity of the two main constituents,  $Cp_2TiCl$  and  $(Cp_2TiCl)_2$ , could be extracted from the knowledge of  $K_8$  and the associated rate constants by analyzing the changes observed in the kinetics upon varying the concentration.<sup>10c</sup> In addition, we succeeded in generating solutions of pure  $Cp_2Ti^+$  [by reacting TlPF<sub>6</sub> with the  $Cp_2TiCl/(Cp_2TiCl)_2$  mixture]<sup>10c</sup> and essentially pure  $Cp_2TiCl_2^-$  (by adding tetrabutylammonium chloride to an electrochemically reduced solution of  $Cp_2TiCl_2$ ,<sup>10b</sup> thus giving access to the relevant rate parameters of these species.

Our analysis presented herein will therefore be based on the very same reaction scheme as elucidated in the Zn-Cp<sub>2</sub>TiCl<sub>2</sub> case,<sup>10c</sup> including now the reactions pertaining to Cp<sub>2</sub>Ti<sup>+</sup>. The overall decay of the different Ti<sup>III</sup> species and the concomitant build-up of Ti<sup>IV</sup> species were followed by UV–vis spectroscopy using different initial concentrations of Zn-Cp<sub>2</sub>TiX<sub>2</sub> (X = Br and I) and excess substrate. The relevant kinetic information was extracted employing the simulation program Gepasi 3.21.<sup>18</sup>

**Benzyl Chloride.** In Figures 5 and 6, some kinetic traces are collected for different concentrations of Zn-Cp<sub>2</sub>TiBr<sub>2</sub> and Zn-Cp<sub>2</sub>TiI<sub>2</sub> in the presence of excess BnCl. The overall kinetics exhibit a weak concentration dependency, because of the influence from the equilibrium reactions. The mechanistic basis for carrying out the fitting procedure consists of eqs 8 and 11–18, which include all relevant reactions involving Cp<sub>2</sub>TiX, (Cp<sub>2</sub>-TiX)<sub>2</sub>, and Cp<sub>2</sub>Ti<sup>+</sup>.<sup>10c</sup>

$$Cp_2TiX + BnCl \xrightarrow{k_{12}} [Cp_2TiX^+ + Cl^- + Bn^{\bullet}] \rightarrow Cp_2TiXCl + Bn^{\bullet}$$
 (12)

$$Cp_2TiX + Bn^{\bullet} \rightarrow [Cp_2TiX^+ + Bn^-] \rightarrow Cp_2TiXBn$$
 (13)

$$(Cp_2TiX)_2 + BnCl \xrightarrow{\kappa_{14}} [(Cp_2TiX)_2^+ + Cl^- + Bn^{\bullet}] \rightarrow Cp_2TiX + Cp_2TiXCl + Bn^{\bullet} (14)$$

$$(Cp_2TiX)_2 + Bn^{\bullet} \rightarrow [(Cp_2TiX)_2^+ + Bn^-] \rightarrow Cp_2TiX + Cp_2TiXBn$$
 (15)

$$Cp_{2}Ti^{+} + BnCl \xrightarrow{k_{16}} [Cp_{2}Ti^{2+} + Cl^{-} + Bn^{\bullet}] \rightarrow Cp_{2}TiCl^{+} + Bn^{\bullet} \xrightarrow{Metal halide} Cp_{2}TiXCl + Bn^{\bullet}$$
(16)

$$Cp_{2}Ti^{+} + Bn^{\bullet} \rightarrow [Cp_{2}Ti^{2+} + Bn^{-}] \rightarrow Cp_{2}TiBn^{+} \xrightarrow{Metal halide} Cp_{2}TiXBn (17)$$

$$Cp_2TiXBn + BnCl \rightarrow Cp_2TiXCl + Bn_2$$
 (18)

In the actual electron transfer steps between  $Cp_2TiX$ ,  $(Cp_2TiX)_2$ , or  $Cp_2Ti^+$  and BnCl depicted in eqs 12, 14, and 16 the benzyl radical, Bn•, is formed along with chloride. Chloride will be captured immediately by  $Cp_2$ -TiX<sup>+</sup>,  $(Cp_2TiX)_2^+$ , or  $Cp_2Ti^{2+}$  to afford  $Cp_2TiXCl$  (besides  $Cp_2TiX$  in eq 14), as revealed by the cyclic voltammetric

<sup>(16)</sup> As shown in our previous paper<sup>10b</sup>  $Cp_2TiCl_2^-$  can be made the main constituent in any of the Met- $Cp_2TiCl_2$  solutions upon addition of tetrabutylammonium chloride.

<sup>(17)</sup> Handbook of Chemistry and Physics, 72nd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, 1991.

<sup>(18)</sup> Mendes, P. *Gepasi*, version 3.21; Virginia Tech: Blacksburg, VA, 1996–1999. The program may be downloaded from the Internet at http://www.gepasi.org.



**Figure 5.** Kinetic traces (absorption vs time) recorded for the buildup of  $Ti^{IV}$  at a wavelength  $\lambda = 535$  nm in THF for the reactions of 87 mM BnCl with (a) 1.0, (b) 2.0, and (c) 5.0 mM solutions of Zn-Cp<sub>2</sub>TiBr<sub>2</sub>. The dotted curves are the best fits based on simulation of eqs 8 and 11–17.



**Figure 6.** Kinetic traces (absorption vs time) recorded for the buildup of  $Ti^{IV}$  at a wavelength  $\lambda = 535$  nm in THF for the reactions of 87 mM BnCl with (a) 1.0 and (b) 2.0 mM solutions of Zn-Cp<sub>2</sub>TiI<sub>2</sub>. The dotted curves are the best fits based on simulation of eqs 8 and 11–17.

analysis. Note that in eq 16 additional halide transfer from the metal halides is included to account for the formation of this product. In principle, the electron transfer and the chloride transfer might take place concertedly, which is the reason for showing the initial products within brackets. Bn• is further reduced to the benzyl anion, Bn<sup>-</sup>, in a fast second electron transfer process shown in eqs 13, 15, and 17, and as this anion is expected to be a strong ligand, we suggest that Cp<sub>2</sub>-TiXBn is formed (possibly concertedly). In the final step, eq 18, Cp<sub>2</sub>TiXBn reacts in a slow process with another molecule of BnCl to afford bibenzyl, Bn<sub>2</sub>, as the final product in accordance with experimental observations.<sup>10c,19</sup>

On the basis of the above reaction scheme, a consistent set of data could be extracted from the best fits as depicted in Figures 5 and 6. The reactions of eqs 13, 15, and 17 were assumed to be fast, so that their only influence on the kinetics would be through the stoichiometry. In contrast, the reaction in eq 18 being slow

Table 3. Rate Constants  $k_{12}$ ,  $k_{14}$ ,  $k_{16}$ ,  $k_{19}$ ,  $k_{20}$ , and  $k_{21}$  for the Reactions between Ti<sup>III</sup>-Based Species and Benzyl Chloride or Benzaldehyde Measured in THF at 20 °C<sup>a</sup>

	BnCl			PhCHO		
	$rac{k_{12}}{ ext{Cp}_2 ext{TiX}}$	$k_{14}$ (Cp <sub>2</sub> TiX) <sub>2</sub>	$k_{16} \ \mathrm{Cp_2Ti^+}$	$rac{k_{19}}{ ext{Cp}_2 ext{TiX}}$	$k_{20}$ (Cp <sub>2</sub> TiX) <sub>2</sub>	$k_{21} \ \mathrm{Cp}_2\mathrm{Ti}^+$
$\overline{\mathbf{X} = \mathbf{Cl}^b}$	0.66	0.80	0.44	<2	70 70	~
X = Br X = I	$\begin{array}{c} 0.65\\ 0.60\end{array}$	$\begin{array}{c} 0.60\\ 0.70\end{array}$	$\begin{array}{c} 0.44 \\ 0.44 \end{array}$	5 C	70 c	$\frac{5}{c}$

 $^a$  All rate constants are given in units of M^{-1} s^{-1}\!.\,^b From ref 10c.  $^c$  Measurements were irreproducible.

could be excluded from the kinetic analysis. Furthermore, the rate constant  $k_{16}$  was fixed at 0.44 M<sup>-1</sup> s<sup>-1</sup> as determined elsewhere.<sup>10c</sup> Attempts to encompass a situation in the simulations where the reactivity of the dimer would be negligible and the monomer with its free coordination site the only reactive species, lowered the quality of the fits.

The extracted data are collected in Table 3 along with data obtained previously for Zn-Cp<sub>2</sub>TiCl<sub>2</sub>. The conclusion is that the reactivities of Cp<sub>2</sub>TiX, (Cp<sub>2</sub>TiX)<sub>2</sub>, and  $Cp_2Ti^+$  with rate constants of 0.44–0.80 M<sup>-1</sup> s<sup>-1</sup> are largely the same, independent of X. In comparison, it might be mentioned that the reactivity of Cp<sub>2</sub>TiX<sub>2</sub><sup>-</sup> toward BnCl with rate constants of <0.019, <0.12, and  $<0.26 \text{ M}^{-1} \text{ s}^{-1}$  for X = Cl, Br, and I, respectively,<sup>10b</sup> is lower, although Cp<sub>2</sub>TiX<sub>2</sub><sup>-</sup> should be the best electron donor from a thermodynamic point of view. The variation in the  $E^{\circ}$ 's of the species concerned (see Table 1) is thus not reflected in the kinetic features, indicating that the reaction of Cp<sub>2</sub>Ti<sup>+</sup>, in particular, possesses strong inner-sphere character with a substantial stabilization of the transition state. Actually, this does not seem to be an unreasonable interpretation as  $Cp_2Ti^+$  with its positive charge and an easily accessible coordination site would be expected to be capable of interacting with the chlorine atom in benzyl chloride. In this respect, it may seem surprising that  $(Cp_2TiX)_2$ , having no free coordination site (see structure II in Chart 1), should exhibit the same reactivity as Cp<sub>2</sub>TiX. However, as discussed elsewhere<sup>10c</sup> the explanation might reside in the fact that the dimer structure in solution is of the half-open type depicted as III in Chart 1, as this would facilitate the coordination of benzyl chloride. In line with this interpretation, we attribute the low reactivity of Cp<sub>2</sub>TiX<sub>2</sub><sup>-</sup> to its lack of a free coordination site.

**Benzaldehyde.** A series of experiments using different initial concentrations of  $Zn-Cp_2TiX_2$  was carried out on the reactions involving PhCHO. These reactions are of great importance for synthetic purposes, as they present a convenient method for carrying out pinacol couplings to afford vicinal diols<sup>2</sup> as depicted in the generalized reaction sequence shown below.<sup>10c</sup>

The reaction mechanism consists of an initial electron transfer process from  $Cp_2TiX$ , eq 19,  $(Cp_2TiX)_2$ , eq 20, or  $Cp_2Ti^+$ , eq 21, to PhCHO followed by dimerization of the thus formed ketyl radicals, eq 22. Note that additional halide transfer from the metal halides is included in eq 21. The kinetic traces recorded for the different solutions of  $Zn-Cp_2TiBr_2$  are shown in Figure 7.

A characteristic feature of these traces is that the contribution from  $(Cp_2TiBr)_2$  is largest initially, as its

<sup>(19)</sup> Control experiments involving benzyl chloride, ZnI<sub>2</sub>, and Bu<sub>4</sub>NI verified that benzyl chloride would not be converted to benzyl iodide in the Zn-Cp<sub>2</sub>TiI<sub>2</sub> solutions.

Titanocene Halide Promoted Reductions

$$C_{P_2}TiX + PhCHO \xrightarrow{k_{19}} H \xrightarrow{Ph}_{C} C$$
(19)

$$(Cp_{2}TiX)_{2} + PhCHO \xrightarrow{k_{20}} H \xrightarrow{Ph} C + Cp_{2}TiX \qquad (20)$$

$$C_{p_{2}Ti^{+}} + PhCHO \xrightarrow{k_{21}} \begin{bmatrix} Ph \\ H - C \\ C_{p_{2}Ti^{+}O} \end{bmatrix} \xrightarrow{Metal \\ halide \\ C_{p_{2}XIIO} \\ H - C \\ C_{p_{2}XIIO} \\ C_{p_{2}XIIO}$$

relative concentration under these conditions is high. As the decay proceeds and the overall concentration of the Ti<sup>III</sup>-based species diminishes, the reactivities of Cp<sub>2</sub>-TiBr and Cp<sub>2</sub>Ti<sup>+</sup> become responsible for the tail of the decay. As seen in Figure 7 reasonable fits can be obtained for the four different concentrations of Zn-Cp<sub>2</sub>-TiBr<sub>2</sub> employed, allowing the extraction of all three rate constants  $k_{19}$ ,  $k_{20}$ , and  $k_{21}$ . In our previous study we attempted to study directly the reaction of Cp<sub>2</sub>Ti<sup>+</sup> with PhCHO, but these experiments had to be renounced because of too low reproducibility.<sup>10c</sup> For Zn-Cp<sub>2</sub>TiI<sub>2</sub>, the overall picture is the same as that for Zn-Cp<sub>2</sub>TiBr<sub>2</sub>, although the lack of reproducibility prevented us from extracting reliable rate data. Presumably, this failure should be ascribed to the sensitivity of Zn-Cp<sub>2</sub>TiI<sub>2</sub> toward the presence of residual water in THF. However, as inferred from the comparison of traces presented for  $Zn-Cp_2TiBr_2$  and  $Zn-Cp_2TiI_2$  in the inset of Figure 7, it may be concluded that the overall reactivity of the latter solution with its higher concentration of Cp<sub>2</sub>Ti<sup>+</sup> is slightly lower.

The extracted rate data are gathered in Table 3 along with data obtained previously for  $X = Cl.^{10c}$  Overall, we find that the reactions of PhCHO are faster than those of BnCl, which is consistent with a larger inner-sphere character in the former case because of the oxophilicity of titanium complexes. The rate constants for Cp<sub>2</sub>TiX and  $(Cp_2TiX)_2$  are by and large independent of X, despite the differences present in the pertinent potentials (approximately 70 mV, see Table 1). Even  $Cp_2Ti^+$ , associated with a high value of  $E^{\circ}$ , exhibits the same reactivity as Cp<sub>2</sub>TiBr. However, the reactivity of (Cp<sub>2</sub>-TiBr)<sub>2</sub> surpasses that of Cp<sub>2</sub>TiBr and Cp<sub>2</sub>Ti<sup>+</sup> by a factor of 14. For the Zn-Cp<sub>2</sub>TiCl<sub>2</sub> solution the rate difference between  $(Cp_2TiCl)_2$  and  $Cp_2TiCl$  is found to be even larger, constituting at least a factor of 35.<sup>10c</sup> These results might be interpreted as if the structure of the dimer indeed is of the half-open type **III** with its easily accessible coordination site rather than the symmetric structure II.

#### **Diastereoselectivities**

The cyclic voltammetric and kinetic investigations indicate that trinuclear complexes (IV in Chart 1) are not involved in the electron transfer step in the pinacol



**Figure 7.** Kinetic traces (absorption vs time) recorded for the decay of Ti<sup>III</sup> at a wavelength  $\lambda = 800$  nm in THF for the reactions of 15 mM PhCHO with (a) 1.0, (b) 2.0, (c) 4.0, and (d) 8.0 mM solutions of Zn-Cp<sub>2</sub>TiBr<sub>2</sub>. The dotted curves are the best fits based on simulation of eqs 8, 11, and 19–21. Inset: Kinetic traces (absorption vs time) recorded for the decay of Ti<sup>III</sup> at a wavelength  $\lambda = 800$  nm in THF for the reactions of 15 mM PhCHO with 2.0 mM solutions of (e) Zn-Cp<sub>2</sub>TiBr<sub>2</sub> and (f) Zn-Cp<sub>2</sub>TiI<sub>2</sub>. The final absorption, *Abs*<sub>final</sub>, has been used as zero point.

coupling reaction of benzaldehyde as shown in eqs 19-21. On the other hand, these results do not provide direct information on the actual coupling step in eq 22, which preferentially leads to the formation of the *dl*isomer. In the literature three main mechanisms based on product formation studies have been proposed for explaining the diastereoselective outcome of such pinacol couplings of aryl and alkyl aldehydes as shown in Scheme 2.<sup>20</sup> In the first case, coordination of both ketyl oxygens to the same Lewis acidic metal center would promote a pseudo-intramolecular diradical coupling, which in turn leads to the preferential formation of the dl-isomer for sterical reasons.<sup>21</sup> The transition state involving trinuclear complexes represents a modification of this mechanism as illustrated in Scheme 3 (with X = Cl).<sup>22</sup> This structure has been proposed in two variants, either as two pentacoordinated Ti<sup>IV</sup> atoms<sup>2a,i</sup> or as tetracoordinated centers where two of the chlorines from the original trimetallic complex have been substituted by oxygen upon reduction of benzaldehyde to a diketyl intermediate.<sup>2c,d,23</sup>

The second but closely related mechanism in Scheme 2 involves addition of a ketyl radical to a metalcomplexed carbonyl species. In the case where the same metal center is implicated, a similar stereochemical preference for the dl-isomer would be predicted. Typically, this mechanism has been proposed for intra-

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Scheme 2. Mechanisms Proposed for Low-Valent Transition Metal-Promoted Pinacol Coupling Reactions Ketyl radical coupling Ketyl radical addition Ketyl radical dimerization bridged intermediate



dl-selective

Scheme 3. Mechanism Proposed for the Ti<sup>III</sup>-Promoted Pinacol Coupling Reactions Involving a Trinuclear Complex



Table 4. Ratios of *dl:meso* for the Hydrobenzoin Products Obtained from Stoichiometric Titanocene Halide Promoted Pinacol Couplings of Benzaldehyde in THF<sup>a</sup>

	$\mathbf{X} = \mathbf{Cl}$	X = Br	$\mathbf{X} = \mathbf{I}$
Zn-Cp <sub>2</sub> TiX <sub>2</sub>	97:3	94:6	87:13
$Mn-Cp_2TiX_2$	97:3	95:5	90:10
$Al-Cp_2TiX_2$	97:3	95:5	91:9
$Cp_2TiX_2 + e^{b}$	96:4	94:6	86:14

<sup>*a*</sup> Ratios were determined by <sup>1</sup>H NMR spectroscopy of the crude reaction mixtures. <sup>*b*</sup> Electrochemical reduction of Cp<sub>2</sub>TiX<sub>2</sub> was carried out in the presence of 0.2 M Bu<sub>4</sub>NPF<sub>6</sub>.

molecular pinacol couplings to afford cyclic diols.<sup>1b,24,25</sup> Finally, the third mechanism involves the simple bimolecular dimerization of two metal-complexed ketyl radical intermediates to form the pinacolate.<sup>20,23,24d,26</sup> For sterical reasons one would expect that the preferred product obtained from this mechanism is the *meso*isomer, whereas for the intramolecular pinacol cyclizations to small rings, the major product would be the *trans*-isomer.

To provide further information regarding the mechanism of this Ti<sup>III</sup>-promoted vicinal diol formation, a study was undertaken to measure the diastereoselectivities of the hydrobenzoins obtained from the pinacol coupling of benzaldehyde mediated by Met-Cp<sub>2</sub>TiX<sub>2</sub> and electrochemically reduced Cp<sub>2</sub>TiX<sub>2</sub>, varying both the reducing metal and the halogen. The *dl:meso* ratios are collected in Table 4. These results are supported by an earlier report by Barden and Schwartz, where similar







diastereoselectivities were noted for the dimerization of benzaldehyde with a solution of  $Cp_2TiCl/(Cp_2TiCl)_2$ .<sup>2b</sup>

First of all, it is important to note that on the basis of the mechanistic interpretation outlined in eqs 19-22 the actual coupling step in eq 22 should be independent of whether the active reagent is Cp<sub>2</sub>TiX,  $(Cp_2TiX)_2$ , or  $Cp_2Ti^+$ . This assumption is reinforced by the observation that the same diastereoselectivity is obtained no matter if the electrochemical or metal-based approaches are employed and, furthermore, no matter if the latter procedure is carried out under catalytic or stoichiometric conditions.<sup>1</sup> These results also emphasize that the introduction of any complexes involving a second metal such as the mechanistic proposal in Scheme 3 is not required in order to explain the high dl:meso ratios. On the other hand, we do see a decrease in the selectivity when the halogen is changed from Cl to Br and I.

Interestingly, in a 2001 paper examining the stereoselectivities of Ti<sup>III</sup>-promoted pinacol couplings, Dunlap and Nicholas proposed a mechanism where the coupling reaction proceeds through a dimeric structure as shown in Scheme 4,<sup>2i</sup> since this complex would also lead to the formation of the *dl*-isomer. Although this possibility cannot be excluded, the structure contains pentacoordinated Ti<sup>IV</sup> atoms, which are not very likely considering that species such as  $Cp_2TiCl_2$ ,<sup>27</sup> ( $Cp_2TiCl)_2$ ,<sup>28</sup> ( $Cp_2TiCl)_2MgCl_2$ ,<sup>29</sup> ( $Cp_2TiCl)_2MnCl_2$ ,<sup>12b</sup> ( $Cp_2TiCl)_2ZnCl_2$ ,<sup>12a</sup> Cp<sub>2</sub>TiCl(OMe),<sup>30</sup> and Cp<sub>2</sub>TiCl(OEt)<sup>31</sup> all exhibit distorted tetrahedral coordination around the Ti cores. In addition, the cyclic voltammetric studies indicated that the mechanism for the electrochemical oxidation of (Cp<sub>2</sub>- $TiX_{2}$  included a fast fragmentation of  $(Cp_{2}TiX)_{2}^{+}$ , and it would seem unlikely that such a cleavage reaction should not occur even faster when a ketyl radical anion

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Scheme 5. Newman Projections of Possible Conformers Being Responsible for the Products Formed in the Dimerization of Two Ti<sup>IV</sup>-Bound Ketyl Radicals



is bound to the  $Ti^{IV}$  core.<sup>10b</sup> Finally, electrochemical studies with  $Cp_2TiX_2$  in the presence of excess halide salts have failed to reveal the presence of the pentavalent  $Cp_2TiX_3^-$  species.

On the basis of the above discussion it appears most likely that the coupling step in the titanocene halide promoted pinacol couplings proceeds via the dimerization of two Ti<sup>IV</sup>-bound ketyl radicals in line with the third mechanistic proposal of Scheme 2. Previously, this has also been suggested by Barden and Schwartz.<sup>2b</sup> However, the experimental finding that the major product is the *dl*- rather than the expected *meso*-isomer and that there is a small but evident drop observed in diastereoselectivity when the halogen is changed from Cl to Br and I underlines the importance of the exact nature of the titanocene moiety. The question remains whether this can be attributed to a sterical or possibly an electronic effect in the dimerization step or as a combination of the two effects.

To provide a plausible explanation, which also takes into consideration the halogen effect, we have examined in Scheme 5 the three two-dimensional Newman projections A, B, and C of two approaching TiCp<sub>2</sub>X-bound ketyl radicals in the intermolecular dimerization. On the basis of purely sterical reasons, C leading to the meso-product would seem the most likely candidate, as it clearly must possess the least sterical interactions between the nearing substituents. However, this is contradicted by the experimental observations, suggesting that this transition structure is essentially absent. Instead, we propose that electronic effects may be playing an important role in the coupling step. Examination of the Newman projections **A** and **B** reveals that both possess two aryl groups in a *gauche* relationship, which potentially could provide for an energetically favorable aryl-aryl interaction.<sup>32</sup> Whereas this cannot account for the halogen effect observed for these reactions, structure A reveals an alternative gauche effect between two electronegative substituents, namely that of the two Ti<sup>IV</sup>-alkoxides. Previously, it has been shown that such a stereoelectronic effect can favor a gauche conformation by as much as 1 kcal  $mol^{-1}$  for vicinal fluorine and oxygen substitutents.<sup>33</sup> Although speculative, it could be expected that an increase in the electronegativity of the OTiCp<sub>2</sub>X substituents would occur in the direction going from X = I to Cl. The gauche

effect would hence be greatest for X = Cl, thereby suggesting that projection **A**, which leads to the *dl*-diol, might be a main contender in the C–C bond forming process. It should be noted that the small differences found for the diastereoselectivities upon exchanging the halogens in the Ti<sup>III</sup>-based species would correspond to a variation in the *gauche* effect of less than 1 kcal mol<sup>-1</sup>.

Some support for this hypothesis can be found in the recent work reported from the Itoh group investigating the ability of Cp<sub>2</sub>TiPh to promote inter- and intramolecular pinacol coupling of aldehydes.<sup>23</sup> In conjunction with our hypothesis, it can be expected that the electronegativity of the OTiCp<sub>2</sub>Ph substituent is less than that of the corresponding halogen-containing species. Hence, the diastereoselective outcome of this coupling reaction would also be expected to be lower than for the OTiCp<sub>2</sub>X substituent. And indeed, a *dl:meso* ratio of 67:33 was observed for the benzohydroin product obtained using Cp<sub>2</sub>TiPh as the reducing agent.

Although sterical effects should not be excluded, the *gauche* effect in pinacol couplings involving ketyl radical dimerization with noncoordinating metal centers could play an important role in dictating the stereochemical outcome of the reaction products. Further work will have to be carried out to confirm the role of this stereo-electronic effect in pinacol coupling reactions.<sup>34</sup>

#### Conclusions

The identity of Ti<sup>III</sup> species generated in THF by Znbased reduction of  $Cp_2TiX_2$  (X = Cl, Br, and I) has been clarified by means of cyclic voltammetry and kinetic measurements. It is found that the principal species formed are a mixture of Cp<sub>2</sub>TiX, (Cp<sub>2</sub>TiX)<sub>2</sub>, and Cp<sub>2</sub>Ti<sup>+</sup>, the distribution of which is dependent on the halogen considered. Interestingly, Cp<sub>2</sub>Ti<sup>+</sup> is present in quite substantial amounts only for X = Br and I, whereas it is completely absent for X = Cl. In all three solutions the amounts of Cp<sub>2</sub>TiX and (Cp<sub>2</sub>TiX)<sub>2</sub> are appreciable, being formed in a mixture having a dimerization equilibrium constant of  $(1-3) \times 10^3$  M<sup>-1</sup>. The latter parameter is independent of the metal (Zn, Mn, or Al) and halogen considered, although the dimerization rate constant is 10-25 times larger for X = Br and I than for X = Cl. Standard potentials determined through simulations of the cyclic voltammograms increase for the identified redox couples in the order Cp<sub>2</sub>TiX<sub>2</sub>/Cp<sub>2</sub>- $TiX_2^- \ll (Cp_2TiX)_2^+ / (Cp_2TiX)_2 < Cp_2TiX^+ / Cp_2TiX \ll Cp_2^-$ Ti<sup>2+</sup>/Cp<sub>2</sub>Ti<sup>+</sup>. For a given halogen-containing Ti<sup>III</sup> species a small increase in the standard potentials is seen going from X = Cl to Br and I. From a thermodynamic point of view  $Cp_2TiX_2^-$  is thus expected to be the strongest electron donor among the different Ti<sup>III</sup> species with the halogen effect increasing the electron-donating ability in the order I < Br < Cl. However, on the basis of kinetic measurements the reactivity of  $(Cp_2TiX)_2$  is found to be larger than or comparable to the reactivities

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of Cp<sub>2</sub>TiX and Cp<sub>2</sub>Ti<sup>+</sup> (and much larger than for Cp<sub>2</sub>TiX<sub>2</sub><sup>-</sup>) as assessed in their reactions with benzyl chloride and benzaldehyde. In addition, the rate data are essentially independent of the halogen. Analysis of the diastereoselectivities observed for the hydrobenzoin formation in the titanocene chloride promoted pinacol coupling of benzaldehyde shows a high *dl:meso* ratio of 97:3 with a decreasing trend when X is changed from Cl to Br and I. This effect is explained by means of a *gauche* effect in terms of increased stereoelectronic interactions between the titanocene moieties in the developing Ti<sup>IV</sup>-bound pinacolate of the transition state. All of the reactions studied in this work, in particular those involving benzaldehyde, proceed by inner-sphere electron transfer pathways.

# **Experimental Section**

Materials. Most chemicals were of commercial origin unless otherwise noted. Benzyl chloride and benzaldehyde were vacuum distilled before use. THF was distilled over sodium and benzophenone under an atmosphere of dry nitrogen. Argon (99.99% purity) was passed through a column of  $P_2O_5$  (Sicapent). Tetrabutylammonium hexafluorophosphate, Bu<sub>4</sub>NPF<sub>6</sub>, was prepared from a hot aqueous solution containing tetrabutylammonium hydrogen sulfate and potassium hexafluorophosphate. The precipitate was filtered and recrystallized from ethyl acetate and pentane. Tetrabutylammonium iodide was recrystallized twice using THF, dried under vacuum at 60 °C for 24 h, and stored in a glovebox. All handling of it had to take place in a dry atmosphere because of its hygroscopic properties. Bis(cyclopentadienyl)titanium dibromide, Cp<sub>2</sub>TiBr<sub>2</sub>, was prepared by adding 1.1 equiv of a BBr<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub> solution to Cp<sub>2</sub>TiCl<sub>2</sub> dissolved in CH<sub>2</sub>Cl<sub>2</sub>. Upon 15 min of stirring the solution was evaporated. The red-brown residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and after filtration this solution was evaporated as well. The product was dried under vacuum at 20 °C for 3–4 h.35 Bis(cyclopentadienyl)titanium diiodide, Cp2TiI2, was synthesized using the same procedure as described for Cp<sub>2</sub>TiBr<sub>2</sub> replacing BBr<sub>3</sub> by BI<sub>3</sub>. The Zn- and Mn-Cp<sub>2</sub>TiX<sub>2</sub> solutions were prepared by adding THF to a flask thoroughly flushed with argon and containing Cp<sub>2</sub>TiX<sub>2</sub> besides excess metal. The solutions were stirred for 30 min until a turquoise green color had become apparent. For preparing Al-Cp2TiX2 activation of the aluminum foil using  $Hg(NO_3)_2$  in THF was required. The activated foil was washed three times with THF before use.

**Apparatus.** Most of the electrochemical equipment was home-built, and a description of the experimental setup is provided in ref 36. The working electrode was a glassy carbon disk of diameter 1 mm. The electrode surface was polished using 0.25  $\mu$ m diamond paste (Struers A/S) followed by cleaning in an ethanol bath. The counter electrode was a platinum coil melted into glass, while the reference electrode

consisted of a silver wire in a Pyrex glass tube (diameter = 7 mm) containing 0.02 M Bu<sub>4</sub>NI + 0.2 M Bu<sub>4</sub>NPF<sub>6</sub>/THF. The tube was closed at one end by a porous ceramic material (TZ, Export Technishe Keramik, München). All potentials were reported versus the ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) redox couple, the potential of which was measured to be 0.52 V vs SCE in 0.2 M Bu<sub>4</sub>NPF<sub>6</sub>/THF. All handling of chemicals was performed on a vacuum line, and at no point during the different operations was the interference of oxygen allowed. The ohmic drop was compensated with a positive feedback system incorporated in the potentiostat. The kinetic traces were recorded by means of a fiber-optic spectrometer, model S1000 (dip-probe), from Ocean Optics, using a light path length of 1 cm.

**Procedure.** In the cyclic voltammetric experiments 0.77 g of Bu<sub>4</sub>NPF<sub>6</sub> (2.0 mmol) and a small magnetic bar were added to the electrochemical cell. The cell was closed and flushed thoroughly with argon for 10 min. Typically, 9 mL of freshly distilled THF and 1 mL of the appropriate standard solution containing the compound of interest were added to the cell using a syringe, and the solution was stirred for 30 s. All experiments in a series were repeated in order to check the stability of the solution. Special care must be taken when recording voltammograms of the Met-Cp<sub>2</sub>TiX<sub>2</sub> solutions, since the metal ions present may be reduced at low potentials and cause deleterious adsorption of metal on the electrode surface. In general, potentials below -1.4 V vs Fc<sup>+</sup>/Fc should be avoided. At the end of each series of experiments a small amount of ferrocene was added, and the potential of the Fc<sup>+</sup>/Fc couple was measured.

In the kinetic experiments, the UV–vis dip-probe was mounted vertically in a two-necked cell containing a small magnetic bar.<sup>36</sup> The cell was closed and flushed with argon for 10 min before 9 mL of freshly distilled THF was added. From a standard solution containing the appropriate Met-Cp<sub>2</sub>-TiX<sub>2</sub> typically 1 mL was transferred to the cell. Benzyl chloride or benzaldehyde was added in excess, while the solution was stirred vigorously. The decay of Ti<sup>III</sup> at the wavelength  $\lambda = 800$  nm and the concomitant buildup of Ti<sup>IV</sup> at  $\lambda = 535$  nm were followed. In the kinetic analysis it was assumed that the extinction coefficients  $\epsilon$  for the different Ti<sup>III</sup> ( $\epsilon \approx 50$  and 45 M<sup>-1</sup> cm<sup>-1</sup> for X = Br and I, respectively) and Ti<sup>IV</sup> species ( $\epsilon \approx 400$  and 700 M<sup>-1</sup> cm<sup>-1</sup> for X = Br and I, respectively) would be the same. In comparison, the corresponding values for X = Cl are  $\epsilon \approx 45$  and 200 M<sup>-1</sup> cm<sup>-1</sup>, respectively.

The diastereoselectivities obtained in the pinacol coupling reactions between benzaldehyde and a stoichiometric amount of the  $Ti^{III}$ -containing species were after acidic workup determined by <sup>1</sup>H NMR spectroscopy.<sup>2b</sup>

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**Supporting Information Available:** Text giving a description of the model parameters used in the simulations and a compilation of cyclic voltammograms of  $Zn-Cp_2TiX_2$  along with relevant fits. This material is available free of charge via the Internet at http://pubs.acs.org.

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