

Characterization of HMPA-Coordinated Titanium(III) Species in Solutions of Zinc-Reduced Titanocene Dihalides

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The effect of adding HMPA to THF solutions of metal-reduced titanocene dihalides (Cp_2TiX_2) has been investigated by means of cyclic voltammetry and kinetic measurements. It is shown that the high coordination affinity of HMPA toward the titanium nucleus results in the formation of a mixture of mainly $\text{Cp}_2\text{Ti}(\text{hmpa})^+$, $\text{Cp}_2\text{Ti}(\text{hmpa})_2^+$, and $\text{Cp}_2\text{TiX}(\text{hmpa})$ with an increase in the amount of ionic constituents as X is changed from Cl to Br and I. The oxidation potentials of all HMPA-coordinated Ti^{III} species are more negative than those of the uncoordinated analogues, but nevertheless an inverse correlation is observed between the HMPA concentration and the rate of reduction of electrophiles such as benzyl chloride and benzaldehyde. This indicates that the reactive reagents in solution remain the uncoordinated Ti^{III} species despite them being in low concentrations. In keeping with this interpretation, HMPA was found to exert no influence on the diastereoselectivity in the pinacol coupling of benzaldehyde.

Introduction

Hexamethylphosphoramide (HMPA) is a highly polar, aprotic solvent that has found widespread use in organic synthesis as a solvent additive. Its usefulness stems from its ability to strongly coordinate to a variety of metal ions, thus affecting reaction rates and pathways.^{1,2} In particular, organolithium reactions benefit greatly by the addition of HMPA, where substantial rate increases can be observed.³ The rates of electron transfer processes from low-valent lanthanide reagents such as SmI_2 are also dramatically increased by the inclusion of HMPA to the reaction mixture.^{4–6} In addition to rate enhancements, the bulky Sm–HMPA complex can increase diastereoselectivities of reductive coupling reactions, as well as stabilize reactive intermediates such as ketyl radicals, thereby preventing competing side reactions (e.g., hydrogen abstraction). Beneficial effects were also discovered in the use of HMPA for the allylation of carbonyl compounds with allyl halides promoted by the low-valent vanadium(II)-based reducing agent $[\text{V}_2\text{Cl}_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$.⁷

In recent years, another popular reducing system based on solutions of metal-reduced titanocene halides (denoted $\text{Met}-\text{Cp}_2\text{TiX}_2$; $\text{Met} = \text{Zn}, \text{Mn}, \text{and Al}$; $\text{X} = \text{Cl}, \text{Br}, \text{and I}$) has found interesting applications in reaction protocols, where stoichiometric amounts of the metal are used to regenerate the titanium catalyst after electron transfer.⁸ In this manner, a variety of synthetically valuable transformations has been accomplished including highly diastereoselective pinacol coupling reactions,⁹ epoxide openings to alkyl radicals,¹⁰ reductions of alkyl halides such as glycosyl bromides¹¹ and *vic*-dibromides,¹² Reformatsky additions,¹³ and others.¹⁴ We have recently published a series of papers dealing with such titanium species, where the main focus was on elucidating the nature of the reactive Ti^{III} species produced in the electrochemical and metal-based reductions of Cp_2TiX_2 in tetrahydrofuran (THF), their reactivities, and their influence on stereochemical aspects of both pinacol couplings of aryl aldehydes and epoxide openings.¹⁵

With the beneficial properties of HMPA on other single-electron reducing agents in mind, we set out to investigate the effect of adding it to solutions of $\text{Zn}-\text{Cp}_2\text{TiX}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$). The study would not only reveal to what extent an electron-donating ligand may influence a synthetically useful reaction such as the pinacol coupling involving benzaldehyde or the reductive dehalogenation involving benzyl chloride but also add to a deeper mechanistic understanding of the Ti^{III} -based

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system. In this analysis, cyclic voltammetric and kinetic measurements were used along with a determination of the diastereoselective outcome in the pinacol coupling reaction.

Results and Discussion

In our previous analyses of THF solutions of Met–Cp₂TiX₂ the principal species formed were identified as a mixture of Cp₂TiX, (Cp₂TiX)₂, and Cp₂Ti⁺, the distribution of which was dependent on the halogen considered.^{15d} For example, Cp₂Ti⁺ 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 Cp₂TiX and (Cp₂TiX)₂ are appreciable, being

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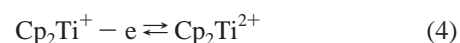
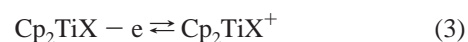
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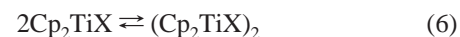
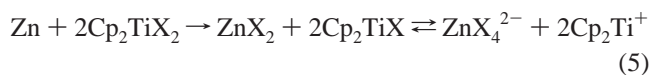
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formed in a mixture having a dimerization equilibrium constant in the range $(1-3) \times 10^3 \text{ M}^{-1}$, a value that is essentially independent of the metal used and the halogen considered. Furthermore, the reactivity of (Cp₂TiX)₂ is larger than or comparable to the reactivities of Cp₂TiX and Cp₂Ti⁺ as assessed in their reactions with benzaldehyde and benzyl chloride. Multinuclear complexes or ionic clusters are not the reacting species in solution¹⁶ despite their isolation and characterization in the solid phase.¹⁷

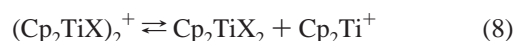
Cyclic Voltammetry. Earlier cyclic voltammetric studies of THF solutions of Met–Cp₂TiX₂ gave immediate access to a characterization of the redox processes shown in eqs 1–4 pertaining to the four species Cp₂TiX₂[–], (Cp₂TiX)₂, Cp₂TiX, and Cp₂Ti⁺.^{15a–d}



It was shown that Cp₂TiX and eventually Cp₂Ti⁺ are generated in either of the metal-induced reductions as depicted in eq 5 for Met = Zn and that (Cp₂TiX)₂ is formed in a reversible dimerization reaction depicted in eq 6, which is independent of the metal.



Figures 1A and 1B present cyclic voltammograms of Zn–Cp₂TiCl₂ recorded in THF solutions in both the presence and absence of HMPA. As discussed elsewhere, when no HMPA is present, the first broad oxidation wave appearing at ca. –0.8 V vs Fc⁺/Fc (abbreviation for ferrocenium/ferrocene) upon increasing the sweep rate actually splits into two waves encompassing the oxidation of both the (Cp₂TiCl)₂ dimer in eq 2 and the Cp₂TiCl monomer in eq 3, i.e., the two constituents in the equilibrium of eq 6 (see Figure 1B). These electrode processes are followed by the chemical reactions, where Cp₂Ti⁺ with the characteristic oxidation wave at –0.4 V vs Fc⁺/Fc corresponding to eq 4 is generated either from a father–son reaction involving Cp₂TiCl and the monomer cation Cp₂TiCl⁺ depicted in eq 7 or from a direct fragmentation of the dimer cation (Cp₂TiCl)₂⁺ depicted in eq 8.



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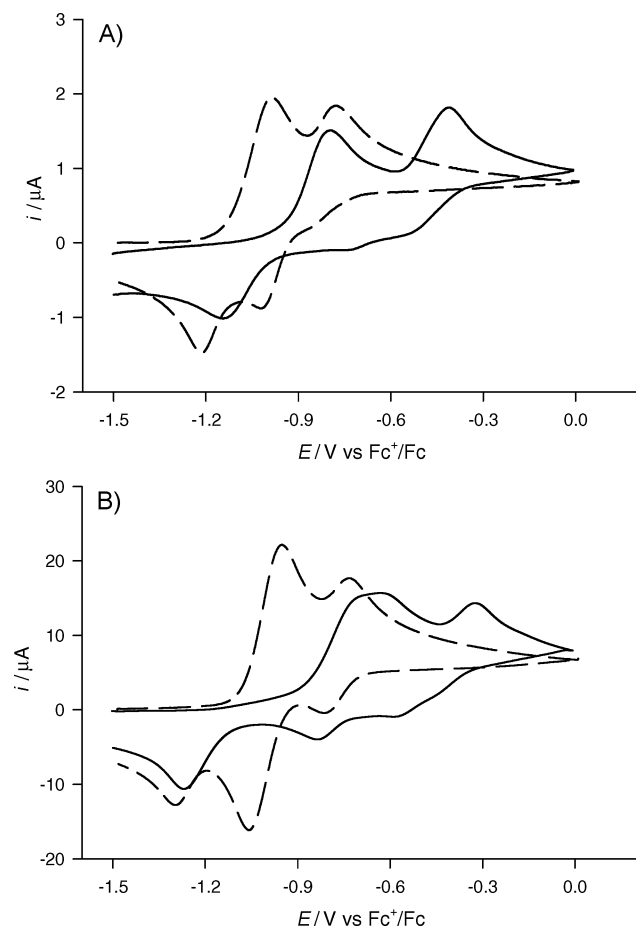


Figure 1. Cyclic voltammograms of 2 mM $Zn-Cp_2TiCl_2$ without (—) and with (---) 100 mM HMPA recorded at sweep rates of (A) 0.1 and (B) 10 $V s^{-1}$ in 0.2 M $TBAPF_6/THF$.

The main peak present on the reverse scan is due to the reduction of Cp_2TiCl_2 (eq 1) produced in the two above reactions or in halide transfer reactions involving the zinc halides. One of the main conclusions from these studies is that Cp_2Ti^+ is not present initially in the $Zn-Cp_2TiCl_2$ solution in contrast to $(Cp_2TiCl)_2$ and Cp_2TiCl ; that is, the equilibrium reaction shown in eq 5 is shifted to the left. On the other hand, in the case of $Zn-Cp_2TiBr_2$ and $Zn-Cp_2TiI_2$ the experimental evidence points to the presence of considerable amounts of Cp_2Ti^+ .^{15c,d}

The effect of adding HMPA to the solutions of $Zn-Cp_2TiCl_2$ is revealed by the cyclic voltammograms included in Figure 1. Clearly, two new waves appear with oxidation potentials that are 200–400 mV lower (i.e., more negative) than the previous ones. Although this effect is smaller than that observed for SmI_2 , where the oxidation peak is shifted by more than 1 V in a negative direction due to a coordination with four HMPA ligands,^{6c} it still indicates that HMPA is coordinated quite tightly to the titanium nucleus. Another interesting observation is that the oxidation wave appearing at approximately -1.0 V vs Fc^+/Fc does not consist of two individual oxidation processes in that no second oxidation peak emerges at high sweep rates (Figure 1B). Thus, it may be concluded that the dimeric $(Cp_2TiCl)_2$ structure breaks up as a result of the interaction with HMPA.

To reveal the identity of the new species formed, cyclic voltammograms were recorded of the three different $Zn-Cp_2TiX_2$ ($X = Cl, Br, I$) solutions containing HMPA. The comparison of the cyclic voltammetric responses shown in Figures 2A and 2B reveals that the second wave is completely independent

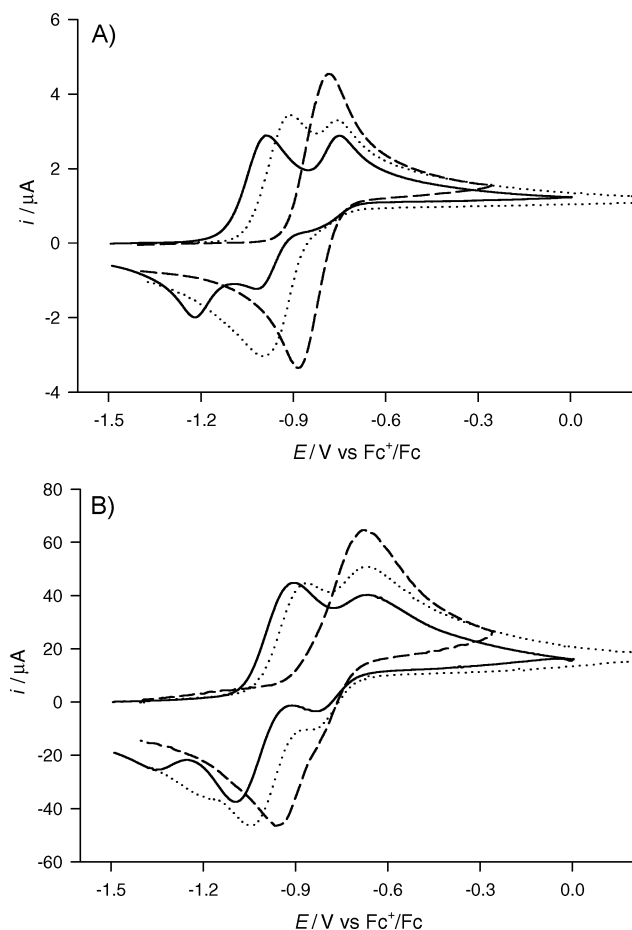


Figure 2. Cyclic voltammograms of 2 mM $Zn-Cp_2TiX_2$, $X = Cl$ (—), Br (····), and I (---), recorded at sweep rates of (A) 0.2 and (B) 50 $V s^{-1}$ with 20 mM HMPA in 0.2 M $TBAPF_6/THF$.

of the halogen, and we therefore assign it to the HMPA-coordinated cation $Cp_2Ti(hmpa)_n^+$ ($n = 1$ or 2). On the other hand, the halogen effect on the first wave is noticeable, which makes us attribute this one to the oxidation of $Cp_2TiX-(hmpa)_n$.¹⁸ The oxidation peak potential increases as X is changed from Cl to Br and I , which is the same order as seen for the $Zn-Cp_2TiX_2$ series in THF alone.^{15d} Actually, in the case of $Zn-Cp_2TiI_2$ the cyclic voltammetric wave of $Cp_2TiI-(hmpa)_n$ almost coincides with that of $Cp_2Ti(hmpa)_n^+$, as envisioned by the presence of the broad oxidation wave on the forward sweep and the prewave feature of the reduction wave on the reverse sweep (see Figure 2B). Note also that the stabilizing effect exerted by HMPA is so strong that the oxidized HMPA-coordinated Ti^{IV} species generated at the surface on the forward sweep can be detected on the reverse sweep, in particular at high sweep rates. In a THF solution the conversion of these oxidized species to Cp_2TiX_2 through eqs 7 and 8 or by reactions involving zinc halides is usually so fast that the peak pertaining to Cp_2TiX_2 is the main feature of the reductive sweep. In the presence of HMPA this peak is hardly observable except for $X = Cl$ (appearing at ca. -1.3 V vs Fc^+/Fc ; see Figures 1 and 2).

Another interesting observation is that the peak current ratio of the two oxidation waves in the case of $X = Cl$ increases as a function of sweep rate in favor of the oxidation of Cp_2TiX-

(18) In a study of the electrochemical reduction of Cp_2TiCl_2 in solvents such as *N,N*-dimethylformamide and pyridine, the solvent coordination issue has been addressed briefly; see: Mugnier, Y.; Moise, C.; Laviron, E. *J. Organomet. Chem.* **1981**, *204*, 61.

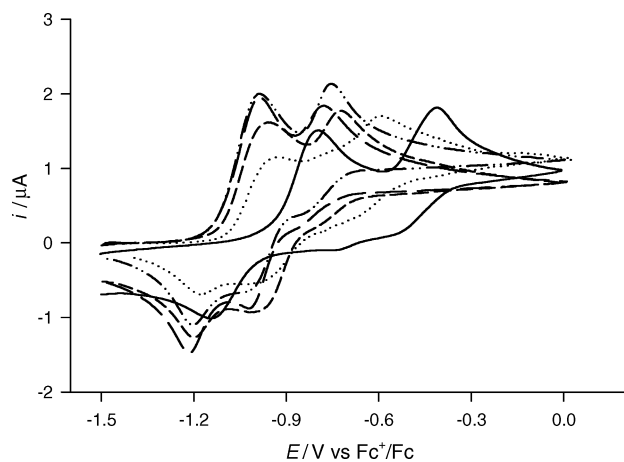


Figure 3. Cyclic voltammograms of 2 mM Zn–Cp₂TiCl₂ recorded at a sweep rate of 0.1 V s⁻¹ with HMPA concentrations of 0 (—), 2 (···), 4 (---), 20 (— · —), and 100 mM (—) in 0.2 M TBAPF₆/THF.

(hmpa)_n; the opposite is true for X = Br and I. With the fast-sweep experiments providing the best picture of the actual solution constitution, such a behavior may be interpreted as Cp₂TiCl(hmpa)_n is the main component of Zn–Cp₂TiCl₂ with Cp₂Ti(hmpa)_n⁺ being mainly generated in fast follow-up processes occurring during the sweep, such as the father–son reaction given in eq 7. In contrast, for the solutions of Zn–Cp₂TiBr₂ and Zn–Cp₂TiI₂ the initial content of Cp₂Ti(hmpa)_n⁺ is appreciable. These results are in keeping not only with the lowering of the titanium–halogen bond energy in the order X = Cl, Br, and I¹⁹ but also with the results we previously have obtained for the Zn–Cp₂TiX₂ solutions.^{15d} Here it was found that Cp₂Ti⁺ is present in quite substantial amounts for X = Br and I but absent for X = Cl. Moreover, a comparison of the peak current ratios in these two studies indicates that HMPA causes a further increase of the ionic character of the solutions.

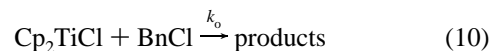
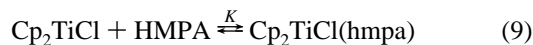
To determine the stoichiometry for the Cp₂TiX(hmpa)_n and Cp₂Ti(hmpa)_n⁺ species, a series of voltammograms was recorded at a sweep rate of 0.1 V s⁻¹ for various equivalents of HMPA added (0, 1, 2, 10, and 50), as shown for X = Cl in Figure 3. The first wave assigned to Cp₂TiX(hmpa)_n shifts by ca. 120 mV in a negative direction upon addition of 1 equiv of HMPA; the effect of additional HMPA is almost negligible. On this basis we conclude that the value of *n* for Cp₂TiX(hmpa)_n is 1. In comparison, the Cp₂Ti(hmpa)_n⁺ wave moves in two steps by –200 and –190 mV, respectively, upon addition of 1 and >2 equiv of HMPA, respectively. This indicates that both Cp₂Ti(hmpa)⁺ and Cp₂Ti(hmpa)₂⁺ may exist, depending on the HMPA concentration. At low concentration Cp₂Ti(hmpa)⁺ is the principal cationic species, but if sufficiently large amounts of HMPA are added, it may be transformed to Cp₂Ti(hmpa)₂⁺. From a chemical point of view this does not seem unreasonable, considering that Cp₂Ti⁺ in contrast to Cp₂TiX has two free coordination sites. It should be emphasized that Cp₂Ti(hmpa)₂⁺ is formed in an equilibrium reaction with Cp₂Ti(hmpa)⁺, the existence of which is revealed by the fact that the wave of the latter reappears in cyclic voltammograms recorded at higher sweep rates (not shown). Because of the great complexity of the underlying reaction mechanism involving a number of ligand transfer reactions, we did not attempt to determine the actual solution constitution through simulation of the cyclic voltammograms.

(19) *Handbook of Chemistry and Physics*, 72nd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, 1991.

Kinetic Studies. The cyclic voltammetric studies revealed that there is a strong interaction between HMPA and the titanocene species. Not only does the coordination of the Lewis base cause a breakup of the dimeric structure and formation of species such as Cp₂TiX(hmpa), Cp₂Ti(hmpa)⁺, and Cp₂Ti(hmpa)₂⁺, but equally important it significantly lowers the oxidation potentials of the Ti^{III} complexes. Thus from a thermodynamic point of view, the addition of HMPA is expected to increase appreciably the electron-donating abilities of the titanocene species in solution. To investigate if this effect also comes through kinetically, the impact of HMPA on the reactions of Zn–Cp₂TiX₂ with both benzyl chloride (BnCl) and benzaldehyde (PhCHO) was studied by means of UV–vis spectroscopy (see Experimental Section). The substrates were added in excess, and the observable rate constants *k*₁ (in the presence of HMPA) were determined assuming pseudo-first-order conditions. Although this is not a truly correct procedure because of the involvement of several Ti^{III}-based species in the complex reaction scheme, it serves well our purposes of revealing changes in the overall reactivity.

The noticeable trend observed in the kinetic data collected in Figures 4A and 4B is the strongly decelerating effect exerted by HMPA on the reaction rates for all three Zn–Cp₂TiX₂ solutions, in particular for X = I and with PhCHO as substrate. Note that *k*₀ refers to the rate constant measured in the absence of HMPA and that two of the measurements for the reaction between Zn–Cp₂TiI₂ and PhCHO are close to the lower limit of measurable rate constants as determined from stability measurements on Zn–Cp₂TiX₂ solutions; that is, the reactivity in these specific cases may be even lower. A likely interpretation of the continuous decrease in the reaction rates upon addition of HMPA is that the formation of Cp₂TiX(hmpa), Cp₂Ti(hmpa)⁺, and Cp₂Ti(hmpa)₂⁺ from the coordination of (Cp₂TiX)₂/Cp₂TiX/Cp₂Ti⁺ with HMPA occurs in equilibrium processes, in which the uncoordinated Ti^{III} species are the only reactive ones. As the equilibrium concentrations of these reagents diminish in the presence of HMPA, the overall reactivity decreases. Clearly, such results are in contrast to the well-known accelerating effect HMPA exerts on SmI₂.^{6c}

On a more detailed level of description, the kinetic measurements may provide information about the composition of the systems studied. First, it may be noted that the relative rate changes are larger if PhCHO rather than BnCl is used as substrate (see Figure 4A). For BnCl the slope (–0.84) determined from linear least squares regression analysis is close to –1, which would suggest that the reaction scheme in this case essentially consists of eqs 9 and 10.²⁰



The above reaction scheme leads to the simple relationship *k*₁/*k*₀ = (*K*[HMPA])⁻¹ (assuming that the steady-state assumption can be applied to Cp₂TiCl and that the forward reaction in eq 9 is faster than eq 10). On this basis *K* may be extracted to be 400 M⁻¹ from the intercept value in Figure 4A. At least for high excesses of HMPA this means that the concentration of Cp₂TiCl will be so low that the dimerization reaction in eq 6

(20) Upon the initial electron transfer from Cp₂TiCl to benzyl chloride, a benzyl radical is formed, which presumably is reduced quickly by Cp₂TiCl to afford a Ti^{IV}-coordinated benzyl anion. The latter may be protonated or may react with another molecule of benzyl chloride in relatively slow processes to afford the final products, toluene or bibenzyl.^{15c,d}

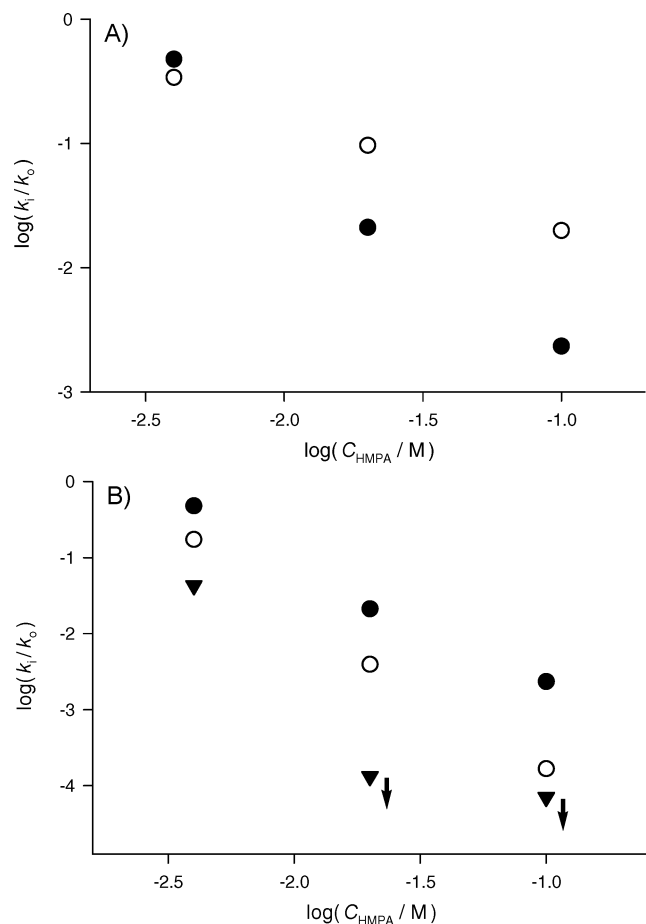


Figure 4. Relative changes in the reaction rate, $\log(k_i/k_0)$, as a function of the concentration of added HMPA, C_{HMPA} , for the reaction of (A) $\text{Zn}-\text{Cp}_2\text{TiCl}_2$ with BnCl (○) and PhCHO (●) and (B) PhCHO with $\text{Zn}-\text{Cp}_2\text{TiX}_2$, $\text{X} = \text{Cl}$ (●), Br (○), and I (▼). For the reaction between $\text{Zn}-\text{Cp}_2\text{TiX}_2$ and PhCHO $k_0 = 30$ ($\text{X} = \text{Cl}$), 23 ($\text{X} = \text{Br}$), and $19 \text{ M}^{-1} \text{ s}^{-1}$ ($\text{X} = \text{I}$). For the reaction between $\text{Zn}-\text{Cp}_2\text{TiCl}_2$ and BnCl $k_0 = 0.4 \text{ M}^{-1} \text{ s}^{-1}$. The uncertainty on the rate constant determination is estimated to be 20%.

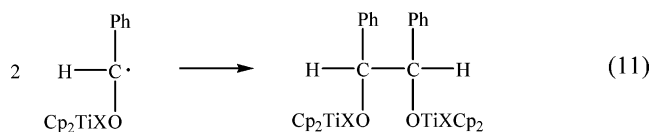
and thus the reactivity of $(\text{Cp}_2\text{TiCl})_2$ become of minor importance. The rate constant of $8.5 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ determined at the highest HMPA concentration can be used as a limiting value for the reactivity of $\text{Cp}_2\text{TiCl}(\text{hmpa})$, a value that is significantly smaller than the 0.80 and $0.66 \text{ M}^{-1} \text{ s}^{-1}$ determined for $(\text{Cp}_2\text{TiCl})_2$ and Cp_2TiCl , respectively.^{15c}

For the reaction involving PhCHO the reactivity of the dimer has previously been found to be much higher than that of the monomer (rate constant ratio >35).^{15c} The expectation is therefore that the reactivity of the dimer has to be specifically accounted for at low HMPA concentrations, whereas its importance should diminish at higher concentrations with less uncoordinated Ti^{III} species present. The consequence should be a larger influence of HMPA on the relative rates, which indeed is expressed by the experimental finding of a numerically larger slope of the pertinent plot ($=1.71$) in Figure 4A. Addressing next the halogen effect, we propose that the larger reactivity changes seen for $\text{X} = \text{Br}$ and in particular I (Figure 4B) should be attributed to the more profound ionic nature of these solutions and the fact that the reactive Cp_2Ti^+ becomes coordinated by HMPA to afford the unreactive $\text{Cp}_2\text{Ti}(\text{hmpa})^+$ and $\text{Cp}_2\text{Ti}(\text{hmpa})_2^+$.

On this basis, it may be concluded that even though HMPA enhances the driving force of the reactions involving Ti^{III} reagents, the shielding effect arising from its coordination to

the titanium nucleus prevents a strong interaction with the substrates in the transition state. In other words, the inner-sphere character of the electron transfer processes of the Ti^{III} species diminishes upon coordination with HMPA to a much larger extent than observed for Sm^{II} in the corresponding SmI_2-HMPA complexes.^{6c}

Diastereoselectivities. In our previous studies the pinacol coupling reaction between $\text{Met}-\text{Cp}_2\text{TiX}_2$ and PhCHO was investigated in detail.^{15d} It was concluded that the actual C–C bond forming coupling step shown in eq 11 consisted of a dimerization of two Ti^{IV} -bound ketyl radicals formed through a reduction of benzaldehyde by Ti^{III} .



The coupling step was shown to be independent of whether the active reagent was $(\text{Cp}_2\text{TiX})_2$, Cp_2TiX , or Cp_2Ti^+ . Since the kinetic results reported above suggested that the reactive species in HMPA-containing solutions should be the uncoordinated Ti^{III} species rather than $\text{Cp}_2\text{TiX}(\text{hmpa})$, $\text{Cp}_2\text{Ti}(\text{hmpa})^+$, and $\text{Cp}_2\text{Ti}(\text{hmpa})_2^+$, the diastereoselectivities would be predicted to be unaffected by the presence of HMPA. Indeed, we find that the *dl:meso* ratio of 97:3 for the reaction between $\text{Zn}-\text{Cp}_2\text{TiCl}_2$ and PhCHO is completely independent of the concentration of HMPA.

Conclusions

HMPA is shown to be capable of coordinating to the titanium core of $(\text{Cp}_2\text{TiX})_2$, Cp_2TiX , and Cp_2Ti^+ present in zinc-reduced THF solutions of Cp_2TiX_2 . The coordination causes a breakup of the dimeric structure with the main constituents becoming $\text{Cp}_2\text{TiX}(\text{hmpa})$, $\text{Cp}_2\text{Ti}(\text{hmpa})^+$, and $\text{Cp}_2\text{Ti}(\text{hmpa})_2^+$. Cyclic voltammetry shows that there is an increase in the amount of ionic constituents as X is changed from Cl to Br and I . All HMPA-coordinated Ti^{III} species are characterized by having lower (i.e., more negative) oxidation potentials compared to those of the uncoordinated analogues. From a thermodynamic point of view the expectation is thus that the HMPA-coordinated Ti^{III} species are relatively strong electron donors. Nevertheless, a continuous decrease is seen in the rates of reduction of electron acceptors such as benzyl chloride and benzaldehyde upon increasing the HMPA concentration, while leaving the diastereoselectivity of the pinacol coupling reaction involving benzaldehyde untouched. These results suggest that, despite their low concentrations, the uncoordinated Ti^{III} species are the actual reagents responsible for the electron transfer reactions in HMPA-containing THF solutions of $\text{Zn}-\text{Cp}_2\text{TiX}_2$.

Experimental Section

Chemicals. Most chemicals were of commercial origin unless otherwise noted. Hexamethylphosphoramide (should be handled with caution as it is carcinogenic), benzyl chloride, and benzaldehyde were vacuum distilled before use. Tetrahydrofuran 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_4NPF_6 , was prepared from a hot aqueous solution containing tetrabutylammonium hydrogensulfate and potassium hexafluorophosphate. The precipitate was filtered and recrystallized from ethyl acetate and pentane. Bis(cyclopentadienyl)titanium dichloride, Cp_2TiCl_2 , was recrystallized from toluene. Bis(cyclopentadienyl)-

titanium dibromide, Cp_2TiBr_2 , was prepared by adding 1.1 mL of a 1.0 M $\text{BBr}_3/\text{CH}_2\text{Cl}_2$ solution (1.1 mmol) to 250 mg of Cp_2TiCl_2 (1.0 mmol) in 10 mL of CH_2Cl_2 . After 15 min of stirring the solution was evaporated under reduced pressure. The red-brown residue was redissolved in 20 mL of CH_2Cl_2 , and after filtration this solution was evaporated as well. The product was dried under vacuum at 20 °C for 3–4 h.²¹ Bis(cyclopentadienyl)titanium diiodide, Cp_2TiI_2 , was synthesized using the same procedure as described for Cp_2TiBr_2 replacing BBr_3 by BI_3 . The $\text{Zn}-\text{Cp}_2\text{TiX}_2$ solutions were prepared by adding THF to a flask thoroughly flushed with argon, containing Cp_2TiX_2 and excess zinc. The solutions were stirred for 30 min until a turquoise green color had become apparent.

Apparatus. Most of the electrochemical equipment was home-built, and a description of the experimental setup is provided elsewhere.²² The working electrode was a glassy carbon disk having a diameter of 1 mm. The electrode surface was polished using 0.25 μm diamond paste (Struers A/S) followed by cleaning in an ethanol bath. The counter electrode consisted of a platinum coil melted into glass, while a silver wire in a sintered glass containing THF/0.2 M Bu_4NPF_6 + 0.02 M Bu_4NI served as the reference electrode. All potentials were reported versus the ferrocenium/ferrocene (Fc^+/Fc) redox couple, the potential of which was measured to be 0.52 V vs SCE in THF/0.2 M Bu_4NPF_6 . 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 home-built potentiostat. The kinetic traces were recorded by means of a fiber-optic spectrometer S1000 (dip-probe) from Ocean Optics, using a light path length of 1 cm.²²

Procedures. In the cyclic voltammetric experiments 0.77 g of Bu_4NPF_6 (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. A standard solution of $\text{Zn}-\text{Cp}_2\text{TiX}_2$ containing for example 50 mg (0.20 mmol) of Cp_2TiCl_2 and excess zinc in 10 mL of freshly distilled THF was prepared prior to the

voltammetric experiments. Typically, 1.0 mL (0.020 mmol) of this standard solution was added to the electrochemical cell using syringes. Subsequently, the appropriate amounts of THF and HMPA were added such that the total volume of added solvents (standard solution + HMPA + THF) equaled 10 mL. The solution was stirred for 30 s. Several of the experiments in a series were repeated in order to check the stability of the solution. The variation in the peak currents may amount to as much as 20% from one experiment to another. Care must also be taken when recording voltammograms of the $\text{Zn}-\text{Cp}_2\text{TiX}_2$ solutions, since the zinc ions present may be reduced at low potentials and cause deleterious adsorption of metal on the electrode surface. At the end of each series of experiments a small amount of ferrocene was added and the potential of the Fc^+/Fc couple was measured.

In the kinetic experiments all absorption spectra and traces were recorded by means of a fiber-optic spectrometer. The UV-vis dip-probe was mounted vertically in a two-necked cell containing a small magnetic bar. The cell was closed and flushed with argon for 10 min. A standard solution of $\text{Zn}-\text{Cp}_2\text{TiX}_2$ containing for example 50 mg (0.20 mmol) of Cp_2TiCl_2 and excess zinc in 10 mL of freshly distilled THF was prepared prior to the kinetic experiments. Typically, 1.0 mL (0.020 mmol) of this standard solution was added to the cell using syringes. Subsequently, the appropriate amounts of THF and HMPA were added such that the total volume of added solvents equaled 10 mL. Benzyl chloride or benzaldehyde was added in excess while stirring the solution vigorously. The decay of Ti^{III} at the wavelength $\lambda = 800$ nm was recorded, and in the case of benzyl chloride the concomitant buildup of Ti^{IV} at $\lambda = 535$ nm was also followed. To obtain a rough estimation of the solution reactivity, the kinetics was approximated by a pseudo-first-order rate law: $-\text{d}[\text{Ti}^{\text{III}} \text{ species}]/\text{dt} = \text{d}[\text{Ti}^{\text{IV}} \text{ species}]/\text{dt} = nk_1[\text{Ti}^{\text{III}} \text{ species}][\text{substrate}]$, where $n = 1$ for benzaldehyde and 2 for benzyl chloride.^{15c,d}

The diastereoselectivities obtained in the pinacol coupling reactions between benzaldehyde and a stoichiometric amount of the Ti^{III} -containing species were determined by ^1H NMR spectroscopy after acidic workup.^{9f}

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(22) Pedersen, S. U.; Christensen, T. B.; Thomasen, T.; Daasbjerg, K. *J. Electroanal. Chem.* **1998**, 454, 123.