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RESEARCH ARTICLE

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Understanding the color change of the solutions of Cp_2TiCl upon addition of water

Antonio Rosales Martínez[1] | **Lourdes Enríquez**[2] | **Martín Jaraíz**[2] | **Tanner Thiessen**[3] | **Jaspreet Sidhu**[3] | **J. Scott McIndoe**[3] | **Ignacio Rodríguez-García**[4]

[1]Department of Chemical Engineering, Escuela Politécnica Superior, University of Sevilla, Sevilla, Spain

[2]Department of Electricity and Electronics, University of Valladolid, Valladolid, Spain

[3]Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada

[4]Department of Chemistry and Physics, Research Institute CIAIMBITAL, University of Almería, Almería, Spain

Correspondence
Antonio Rosales Martínez, Department of Chemical Engineering, Escuela Politécnica Superior, University of Sevilla, 41011 Sevilla, Spain.
Email: arosales@us.es

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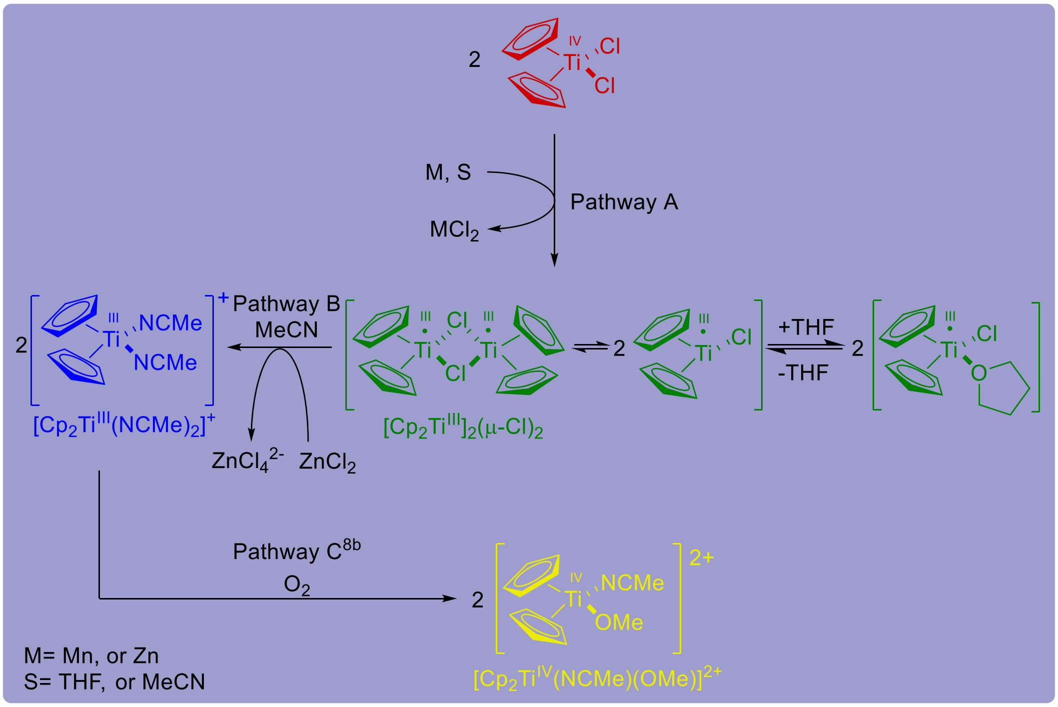
Reduction of red bis (cyclopentadienyl)titanium (IV) dichloride (Cp_2TiCl_2) with manganese dust in dry THF produces a green solution that turns deep blue upon the addition of traces of water. Mass spectrometric analysis and DFT calculations have been performed to achieve a better understanding of the species that may be present after the interaction of water with reduced Cp_2TiCl_2. The deep blue solution provides a handy visual indicator for the qualitative determination of water in THF.

KEYWORDS
colorimetric indicator, hydrogen atom transfer reagent, radical chemistry, titanocene

1 | INTRODUCTION

$Cp_2Ti^{III}Cl$, commonly known as titanocene monochloride, has been recently proposed as a new green reagent that can efficiently catalyze a wide range of synthetic processes, with high diastereo- and regioselectivity, because of its ability as single-electron transfer (SET) complex.[1–10] Because of its high reactivity, it is better to use it freshly prepared by a simple and straightforward reduction of commercial Cp_2TiCl_2 with elemental Mn or Zn.[11–14] Alternatively, electrochemical reduction,[15–17] organosilicon reducing agents,[18] and photoredox catalysis[19,20] can be used to obtain this SET complex from Cp_2TiCl_2. In solution, it exhibits an equilibrium between dinuclear and mononuclear species, as Skrydstrup et al. reported in a study on the nature of this SET complex (Pathway A, Scheme 1).[21]



SCHEME 1 Synthesis and subsequent oxidation of titanocene (III) species in MeCN and THF solution

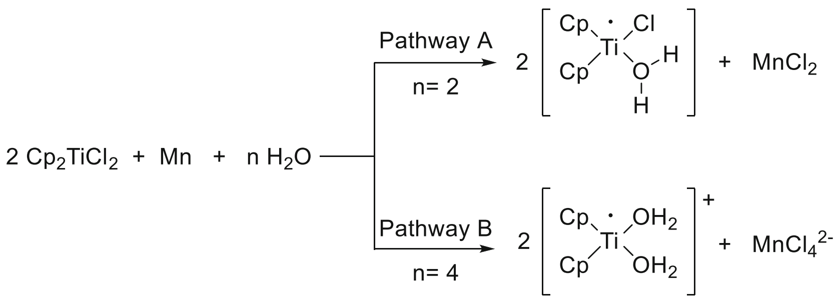
The initial reduction of Cp_2TiCl_2 to the titanocene (III) species can be easily visualized by a change in the color of the solution when Mn or Zn is used as a reducing metal. When THF is the solvent, the initially orange-red solution of Cp_2TiCl_2 turns green after reduction indicating that the titanocene (III) species is formed.[11–14] However, when MeCN is the solvent, the solution finally turns deep blue, as $[Cp_2Ti(NCMe)_2]^+$ is formed[22–24] (Pathway B, Scheme 1). In both cases, oxidation of the titanium (III) species with molecular oxygen generates a yellow solution. This color change has been used as an effective O_2 sensor in inert-atmosphere boxes, because exposition to air of a solution of $[Cp_2Ti(NCMe)_2]^+$ produces a fast color change from blue into bright yellow,[22–24] because of the formation of $[Cp_2Ti(NCMe)(OMe)]^+$ (Pathway C, Scheme 1). This property makes the blue acetonitrile solution a useful visual indicator to detect the presence of trace oxygen.[22]

It has also been reported that in free-radical reactions mediated by this SET complex, water acts as a hydrogen atom donor.[25–27] However, the color changes experienced by the THF solutions of this reagent in the presence of water have not been investigated. Therefore, a study of the molecular species responsible for the visual changes would be desirable, which should increase our knowledge on the active species involved in the hydrogen atom transfer (HAT) processes. In addition, these insights could be useful for the development of a new colorimetric method to qualitatively determine the presence of water in THF.

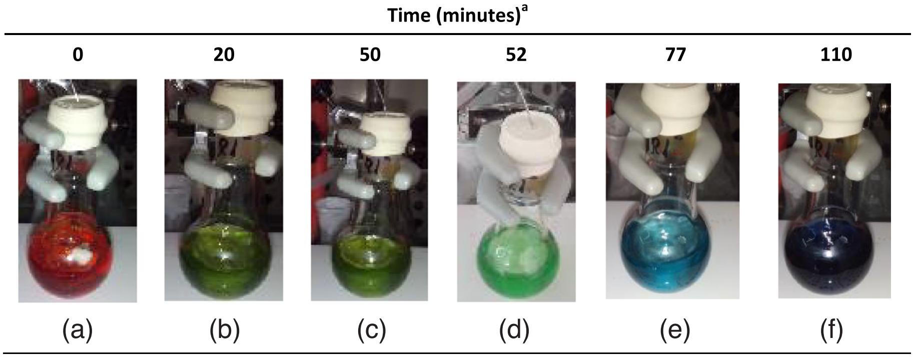
2 | RESULTS AND DISCUSSION

The ability of the water molecule to act as a hydrogen atom transfer reagent can be understood considering the weakening of the H–O bond dissociation energy by about 60 kcal/mol[25] by the presence of $Cp_2Ti^{III}Cl$, which allows the corresponding aqua complex to act as a hydrogen atom donor (Pathway A, Scheme 2). This fact was supported by kinetic measurements. In this way, Newcomb et al.[28] determined the rate constant for the HAT reaction of $Cp_2TiCl–H_2O$ to secondary alkyl radicals. Those results are in good agreement with the experimental fact of water being a good HAT reagent because of the activation of the H–O bond by the titanium system. Later, Gansäuer et. al[27] observed that the initially proposed structure of the titanocene (III)–H_2O complex was not accurate. On the basis of additional results obtained from cyclic voltammetry experiments, electron paramagnetic resonance spectra, and theoretical calculations, a new structure of the titanocene (III)–aqua complex was reported (Pathway B, Scheme 2).

Even though this SET reagent demonstrated for the first time that water is not inert toward free radicals, no attention was paid to the color changes experienced by the THF solutions of titanium. The study of the color changes that can be observed in these titanocene/THF solutions when water is present can be used to gain a better understanding of the different molecular species involved. It could also be used for the development of a



SCHEME 2 Proposed Cp_2TiCl aqua complexes



[a] Water was added after 50 minutes of the addition of THF to the Cp_2TiCl_2+Mn mixture.

FIGURE 1 Color of a Ti (IV) solution in dry THF (a), color of titanium (III) species solutions in dry THF (b, c), and color change observed in the solution when water is added (d, e, f)

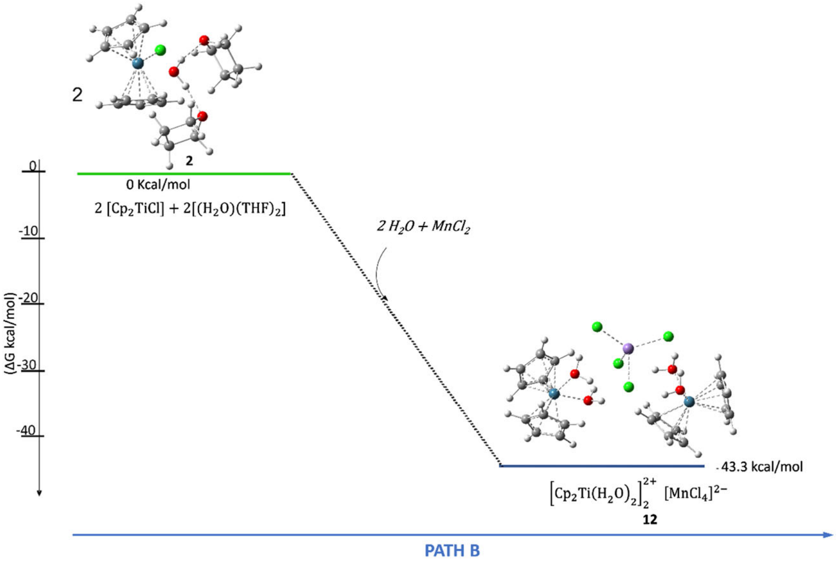


FIGURE 2 Free energy profiles for formation of the titanium aqua complex when water is added (see Data S1 for a more detailed figure).

qualitative colorimetric method for the determination of water in THF.

In this way, upon addition of deoxygenated THF (13 ml) to a mixture of Cp_2TiCl_2 (0.25 mmol) and Mn (0.9 mmol), the initially red-orange solution (Figure 1a) turns lime-green (Figure 1b) after 20 min. If the mixture is kept under an inert atmosphere, the color remains unchanged (Figure 1c). If after stirring this mixture for 30 min, water (8.4 mmol) in THF (2 ml) is added, the lime-green solution turns light green (Figure 1d) in just 2 min. Stirring the reaction mixture under the same conditions slowly transforms the color toward blue tonalities. In this way, 27 min after the addition of water, the solution takes a bluish-green color (Figure 1e). Finally, the solution turns dark blue (Figure 1f).

This striking color change from green to blue provides an immediate signal that new titanium-containing species are being formed. In order to corroborate the interaction of water with titanium (III) species in THF, quantum chemical calculations were carried out using DFT (see Data S2 for details). The results obtained from the computational study of the entire process are summarized in Figure 2 (see Data S1 and Data S2 for details), where Gibbs free energies are in kcal/mol relative to intermediate Cp_2TiCl.

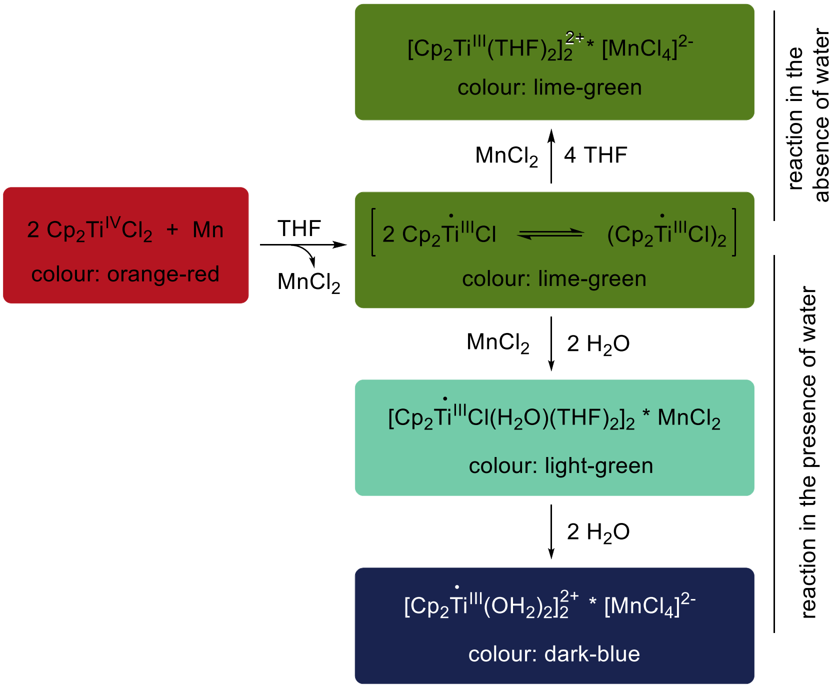
If water is added to the green solution of titanium (III) species in THF (Figure 2; a detailed reaction pathway scheme can be found in Data S2 and Data S1), the reaction evolves through small barriers, by replacing the chlorine atoms with water molecules, resulting the blue solution containing the cation $[Cp_2Ti^{III}(OH_2)_2]^+$. Previous computational results reported by Gansäuer et al.[27] suggested the formation of this cationic titanocene (III) complex in the presence of $ZnCl_2$. However, in dry THF, we tried to model a similar pathway by substituting the chlorine atoms for the oxygen atoms in the solvent (THF). We have found that the Gibbs free energy of this process is $\Delta G = -6.4$ kcal/mol (see Data S2). On the other hand, the reaction in the presence of water, which leads to the formation of $\left[Cp_2Ti^{III}(OH_2)_2\right]_2^{2+}[MnCl_4]^{2-}$ (species **12**, Figure 2), is highly favorable ($\Delta G = -43.3$ kcal/mol for the whole process).

In summary, when water is added, the process evolves through a sequence of low-barrier steps, producing reaction intermediates as a consequence of coordination between Ti (III) and Mn (II) species in which the chlorine atoms directly attached to the titanium are replaced by water molecules. Therefore, the final species **12**, which has no chlorine atoms bound to titanium, could be responsible for the dark blue color of the solution.

Scheme 3 shows the proposed mechanism and color (in the energy levels) of the intermediates of reaction for the reduction of Cp_2TiCl with Mn in dry THF or THF/water. The modeling for the first step in Scheme 3 (reduction of $Cp_2Ti^{IV}Cl_2$ to $Cp_2Ti^{III}Cl$) considering atomic Mn points to an instantaneous conversion. However, the color change from red to green takes 20 min (Figure 1b). The likely cause of the slow reaction is the heterogeneous nature of the reductant, with the reaction rate being controlled by the dissolution of the metallic Mn dust. In addition, considering the proposed sequence for the energetically favorable formation process of the blue cation (Scheme 2), it can be tentatively proposed a color assignment to the main reaction intermediates, as shown in Scheme 3.

After the computational study, we turned to experimental means of probing the reaction solution. Gansäuer et al.[27] proved by EPR spectroscopy and cyclic voltammetry that both neutral and cationic species can be formed in an aqueous solution of THF in Cp_2TiCl. To provide new insights, we turned to electrospray ionization mass spectrometry (ESI-MS). Note that ESI-MS does not provide information on the neutral components of the reaction and does not always retain all ligands throughout the desolvation process, especially those that are only weakly bound.[29] ESI-MS can be run routinely under anaerobic conditions provided suitable precautions are taken.[30]

In the first stage of the reaction (orange/red solution; Figure 1a), no Ti-containing species were observed in the positive or negative ion mode mass spectra (as expected, as reduction has not yet occurred). After the addition of Mn dust and conversion of the solution to lime-green (Figure 1b), we observed new charged species in both the



SCHEME 3 Proposed mechanism and color of the solution for the reduction of Cp_2TiCl_2 with Mn in anhydrous THF and THF/water

positive and negative ion modes. The negative ion mode was dominated by aggregates of the form $[(MnCl_2)_nCl]^-$ ($n = 1$–3; Figure 3a), at m/z 160, 287, and 416, with isotope patterns matching the calculated patterns of those species. Note that because dianionic species have a limited existence in the gas phase (there is no solvent around to stabilize them against loss of X^- or of an electron),[31] we would not expect to observe the dianionic $[MnCl_4]^{2-}$. The abundance of the aggregate ions suggests that there is a substantial amount of neutral $MnCl_2$ present in solution, as expected for the reaction $2Cp_2TiCl_2 + Mn \rightarrow 2Cp_2TiCl + MnCl_2$.

An ion-paired species was also observed with the overall composition $[MnCl_4Cp_2Ti]^-$ at m/z 375, which is probably best thought of as $[(MnCl_3)(Cp_2TiCl)]^-$ and that provides evidence both for the reduction of $Cp_2Ti^{IV}Cl_2$ to $Cp_2Ti^{III}Cl$ and the concomitant oxidation of Mn. Its abundance suggests that there is a considerable amount of neutral $Cp_2Ti^{III}Cl$ present in solution. The m/z 375 ion decomposes in the gas phase under collision-induced dissociation (CID) to $[MnCl_3]^-$ at m/z 161, losing neutral $Cp_2Ti^{III}Cl$, and corroborating the assignment.

The positive ion mode (Figure 3b) was dominated by an ion at m/z 250, which can be assigned to $[Cp_2Ti^{III}(THF)]^+$. This ion likely arises from a loss of halide from $Cp_2Ti^{III}Cl$, a well-known ionization pathway for metal complexes in polar solvents in ESI-MS.[32] It decomposes when fragmented by CID to $[Cp_2Ti]^+$ at m/z 178, that is, loss of neutral THF.

Further analysis of solutions after H_2O addition did not reveal the presence of newly charged Ti-containing species in either ion mode, despite the evident color changes. However, note that both $Cp_2Ti^{III}Cl$ and $[Cp_2Ti^{III}(OH_2)_2]_2^{2+}$ are both likely to provide the same ion in ESI-MS analysis in THF solution, namely, $[Cp_2Ti^{III}(THF)]^+$, because the former can only acquire a charge via chloride ion loss, and the water ligands are unlikely to be tenacious enough binders to survive the

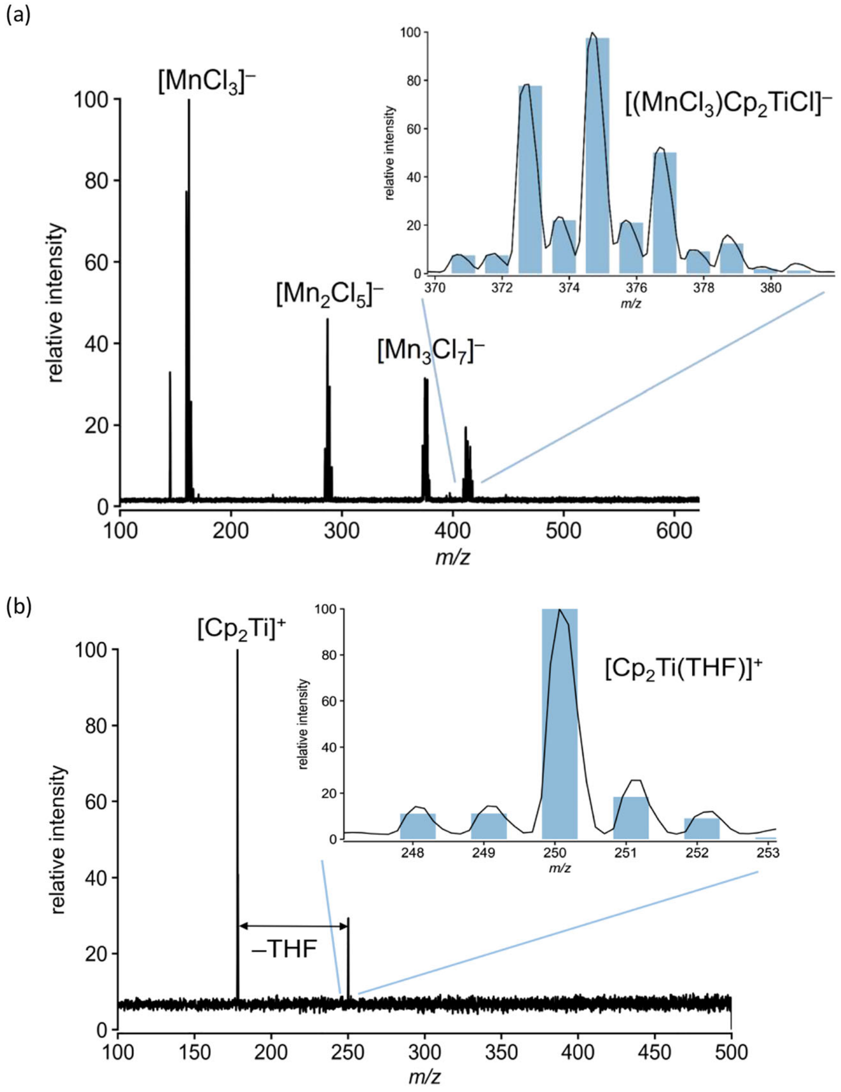


FIGURE 3 Mass spectra of the anhydrous THF solution generated by reduction of Cp_2TiCl_2 with manganese dust. (a) Negative ion mode full spectrum, inset shows experimental and calculated isotope patterns for $[(MnCl_3)Cp_2TiCl]^-$; (b) positive ion mode product ion MS/MS spectrum for $[Cp_2Ti(THF)]^+$, inset shows experimental and calculated isotope patterns for the precursor ion.

TABLE 1 Time evolution of the color of the reaction

Entry	Cp_2TiCl_2(mmol)	Mn(mmol)	Solvent(THF[a] (ml)/H_2O[b] (μL)	Lime-green color (min[d])	Dark blue color (min[d])
1	0.25	0.9	15/152	30	60
2	0.25	0.9	15/75	30	60
3	0.25	0.9	15/38	30	60
4	0.25	0.9	15/19	30	60
5	0.25	0.9	15/9	30	60
6[c]	0.25	0.9	15/0	30	-

[a] THF was dried and distilled from Na/benzophenone under argon and was deoxygenated prior to use.

[b] Water was deoxygenated prior to use.

[c] Continuous green solution after stirring for 5 h.

[d] Time measured from the start of the reaction.

desolvation process. The appearance of THF as a ligand arises because of its large excess, present as it is as a solvent.

This preliminary result provides a solid experimental evidence of the effect of water on the change of color suffered by the initially lime-green titanocene (III) solution in THF. In addition, the change of color is a handy colorimetric visual indicator that allows us to determine the presence of water in THF. For this purpose, the color change of different solutions of titanocene (III) in THF has been monitored. The results are summarized in Table 1. The role played by water was studied by performing a series of five experiments with decreasing amounts of this reagent (Entries 1–5, Table 1). In all cases, the initially green solution of Cp_2TiCl turned dark blue. On the other hand, under a strict absence of water, no dark blue species could be detected even after prolonged reaction times (Entry 6, Table 1). These results confirm that the color of the titanium species in THF can be used as a colorimetric indicator for the qualitative determination of the presence of water in THF. The described procedure permits the determination of the presence of water in THF in concentrations as low as 0.07%.

3 | CONCLUSIONS

In summary, an inexpensive, safe, simple, and green method for the qualitative determination of water in THF based on the color change of green titanocene species to blue solution is described. A detailed experimental study of the effect of water concentration on color change is reported. In addition, a computational investigation confirmed that the final species responsible for the dark blue color of the THF solution when water is present could be $[Cp_2Ti^{III}(OH_2)_2]^+$ $[MnCl_4]^{2-}$ (**12**), and the species formed in anhydrous THF could be $[Cp_2Ti(THF)_2]_2^{2+}$ $[MnCl_4]^{2-}$ (**1**) (green solution). ESI-MS confirmed the presence of $Cp_2Ti^{III}Cl$ through the observation of $[(Cp_2TiCl)(MnCl_3)]^-$ in the negative ion mode and cationic Ti^{III} species through the observation of $[Cp_2Ti(THF)]^+$ in the positive ion mode. This detailed mechanistic investigation offers new advances in radical chemistry catalyzed by titanocene (III), where previously, the influence of other additives has been reported.[33]

4 | EXPERIMENTAL SECTION

4.1 | General methods

Dry THF was prepared by distillation from Na/benzophenone under argon. THF and water were deoxygenated prior to use by bubbling a stream of dry argon. Cp_2TiCl_2 was purchased from Aldrich, and all other reagents, including manganese dust, from Acros and THF (grade HPLC) from VWR. Reactions involving Cp_2TiCl formation were performed under argon.

4.2 | Mass spectrometry general considerations

A Waters Acquity Triple Quadrupole Mass spectrometer was used to measure mass spectra. The instrument was equipped with a Z-Spray pneumatically assisted electrospray ionization source in the positive or negative ion mode. Instrument source parameters were as follows: capillary voltage was held at 3 kV and cone voltage at 15 V. The following settings were used for desolvation conditions: desolvation gas flow rate, 100 L/h; cone gas flow rate, 100 L/h; source temperature, 75°C; and desolvation temperature, 150°C.

4.3 | Color changes observed in Figure 1

THF (13 ml), previously dried and deoxygenated, was added to a mixture of Cp_2TiCl_2 (62.2 mg, 0.25 mmol) and Mn (49.4 mg, 0.9 mmol) under an argon atmosphere, and the suspension was stirred at 25°C. After 20 min, the originally red-orange solution turned green. The mixture was stirred for 30 min, and then water (151.2 mg, 8.4 mmol) in THF (2 ml) was added. Figure 1 shows the time at which the color change appears in the solution.

4.4 | General procedure for results of Table 1

Deoxygenated water (μl; see Table 1) and THF (15 ml) were added to a mixture of Cp_2TiCl_2 (62.2 mg, 0.25 mmol) and Mn (49.4 mg, 0.9 mmol) under an argon atmosphere, and the suspension stirred at 25°C. After 20 min, the initially red-orange solution turned green. After the reaction times indicated in Table 1 for each of the entries, a color change from green to deep blue was observed, except for the reaction carried out in the absence of water, which conserved its green color.

4.5 | Preparation of solutions for MS analysis

One hundred twenty-five milligrams of Cp_2TiCl_2 and 99 mg of Mn dust were added to a 100-ml Schlenk flask in a nitrogen-filled glovebox. The Schlenk flask was removed from the glovebox and attached to a Schlenk line. Twenty-seven milliliters of dried degassed THF were introduced into the flask with the aid of a syringe, and the first MS sample was obtained. Each MS sample was isolated in the same fashion. A glass syringe was purged with nitrogen three times before being used to transfer a sample of the reaction into a 50-ml Schlenk flask, which was then transferred into the glovebox. The solution was gravity filtered into a 3-dram glass vial. One milliliter of this solution was diluted with 4 ml of dried degassed THF before being loaded into a 1-ml plastic syringe. The syringe had a needle attached to the end and was inserted into a rubber stopper to decrease atmospheric contamination while handling outside the glovebox. The syringe and stopper were transferred out of the glovebox and inserted into the injector of MS. The first sample was red and obtained at time 0 min. The original reaction vessel was heated to 25°C; 1.5 h later, the solution was green, and the next MS sample was obtained in the same fashion as before. One milliliter of deionized and degassed water was added to 50 ml of dried degassed THF. Fifteen milliliters of this solution was slowly injected into the reaction vessel causing an almost immediate conversion from green to blue; 2 h later, the solution was blue and the final MS was obtained.

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AUTHOR CONTRIBUTIONS

Antonio Rosales Martínez: Conceptualization; investigation; writing-original draft. **Lourdes Enríquez:** Investigation. **Martín Jaraíz:** Investigation. **Tanner Thiessen:** Investigation. **Jaspreet Sidhu:** Investigation. **J. Scott McIndoe:** Investigation; writing-review and editing. **Ignacio Rodriguez-Garcia:** Investigation; writing-review and editing.

CONFLICTS OF INTEREST

The authors report no declaration of interest.

DATA AVAILABILITY STATEMENT

Data openly available in a public repository that issues datasets with DOIs

ORCID

Antonio Rosales Martínez https://orcid.org/0000-0003-0182-0548
Lourdes Enríquez https://orcid.org/0000-0002-0655-7518
Martín Jaraíz https://orcid.org/0000-0001-6688-3158
Tanner Thiessen https://orcid.org/0000-0001-5187-2093
Jaspreet Sidhu https://orcid.org/0000-0001-7405-9089
J. Scott McIndoe https://orcid.org/0000-0001-7073-5246
Ignacio Rodríguez-García https://orcid.org/0000-0002-2985-8567

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