Electronic Supplementary Information for:

Unprecedented H-Atom Transfer from Water to Ketyl Radicals mediated by Cp_2TiCl.

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General Details. For all reactions using titanocene, solvents and additives were thoroughly deoxygenated prior to use. The next complexes[1] were prepared following reported procedures: $(Cp_2TiCl)_2$ (**8**),[2] $(Cp_2TiCl)_2ZnCl_2$ (**A**),[3] and $(Cp_2TiCl)_2MnCl_2$ (**B**).[3] They are high air-sensitive compounds and it is recommended to be handled in a globes box under Ar atmosphere. Pinacols **3** are known compounds and were isolated as pure samples showing NMR spectra identical to reported data.[4]

General procedure for control experiments. Strictly deoxygenated THF (20 mL) was added under Ar atmosphere to a mixture of titanocene(III) complex (0.3 mmol) and an additive, if is required. A solution of acetophenone (0.6 mmol) in THF (2 mL) was then added. The mixture was stirred for 13 h and then diluted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane mixtures) to give the corresponding products.

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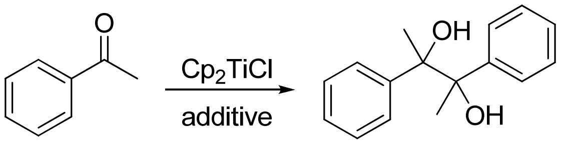
[1] Titanocene(III) is usually formed in situ by reduction of Cp_2TiCl_2 with Mn or Zn dust, and consequently is contaminated by stoichiometric amounts of $MnCl_2$ or $ZnCl_2$. Therefore, we have carried out the spectroscopic study of closely related compounds $(Cp_2TiCl)_2ZnCl_2$ (**A**) and $(Cp_2TiCl)_2MnCl_2$ (**B**).

[2] R. S. P. Coutts, P. C. Wailes and R. L. Martin, *J. Organomet. Chem.* **1973**, *47*, 375-382.

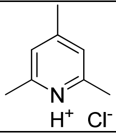
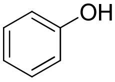
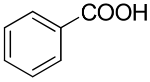
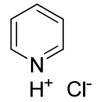
[3] These complexes are prepared from benzene and some co-crystallization benzene molecules are present in the solid sample: D. G. Sekutowsky and G. D. Stucky, *Inorg. Chem.* **1975**, *14*, 2192-2199.

[4] M. Paradas, A. G. Campaña, R. E. Estévez, L. Álvarez de Cienfuegos, T. Jiménez, R. Robles, J. M. Cuerva and J. E. Oltra, *J. Org. Chem.* **2009**, *74*, 3616-3619.

Pinacolization of acetophenone (2) in the presence of different potential H-atom donors.



2 *dl:meso* pinacols (**3**)

Entry	**Additive**	**Yield (%)** **(*dl:meso*)**
1		89 (7:3)
2		60 (3:2)
3		48 (7:3)
4		46 (65:35)

UV-vis spectra of complexes A and B.

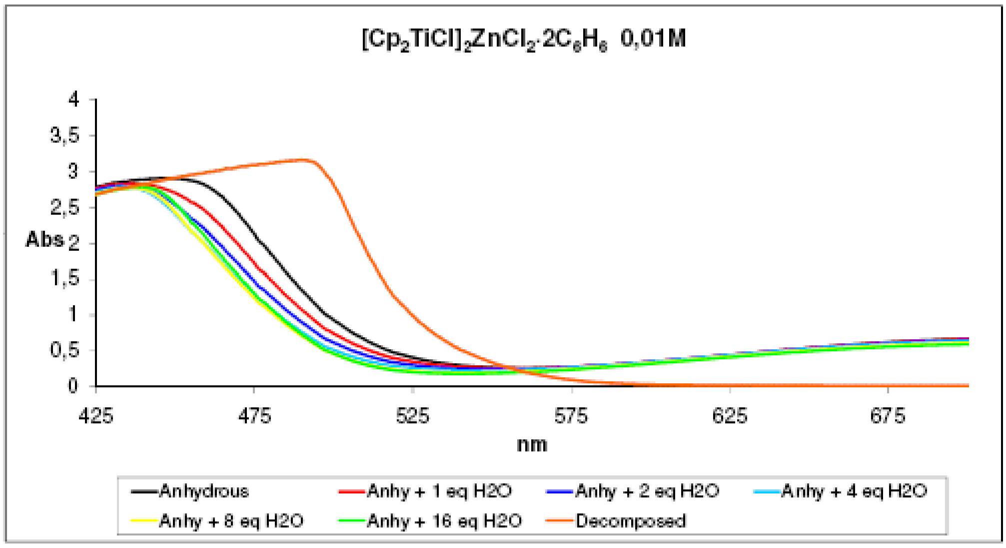


Figure S1. UV-vis spectra of **A** in THF with increasing amounts of H_2O

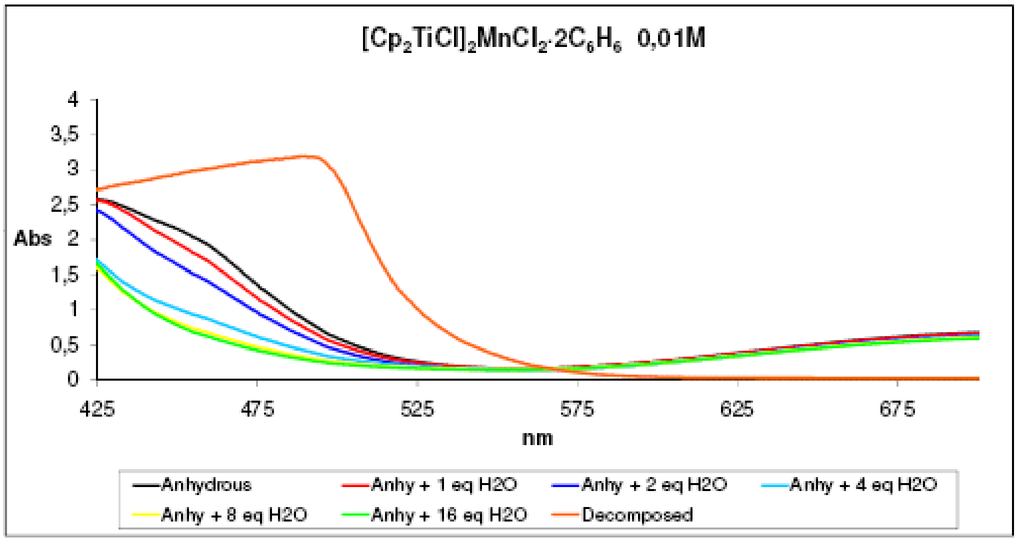


Figure S2. UV-vis spectra of **B** in THF with increasing amounts of H_2O

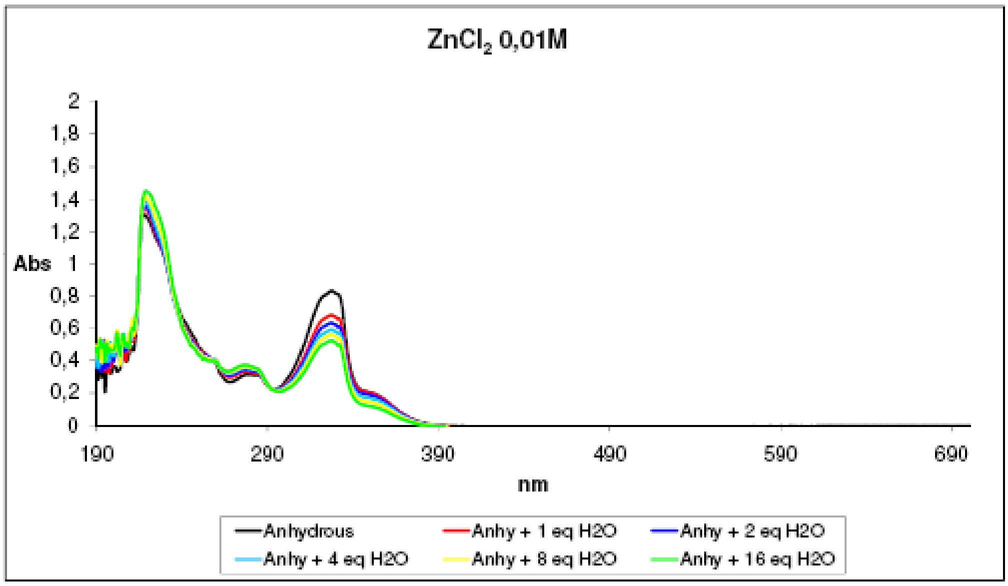


Figure S3. UV-vis spectra of $ZnCl_2$ in THF with increasing amounts of H_2O

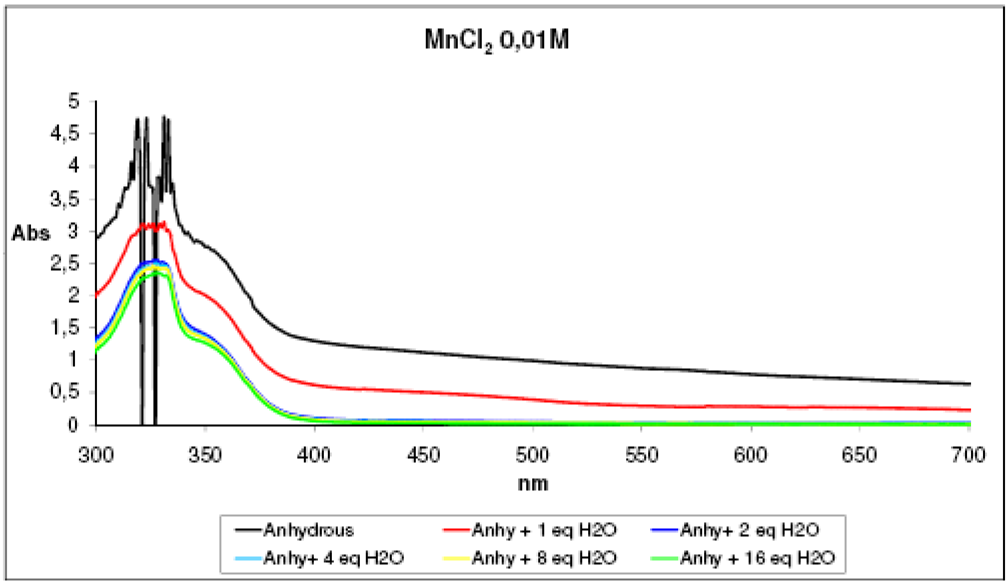


Figure S4. UV-vis spectra of $MnCl_2$ in THF with increasing amounts of H_2O

Control UV-vis spectra.

In the UV-VIS spectra of **8** in THF with 10 equiv of 2,4,6-collidine hydrochloride (Figure S6) and 10 equiv of pyridine hydrochloride (Figure S7) the absorbing wavelength at 450 nm, characteristic of **8**, is retained. The changes in absorbance are due to minor concentration changes during the preparation of the samples. Moreover, both salts are partially insoluble in THF at these concentrations and perfectly clear solutions could not be obtained.

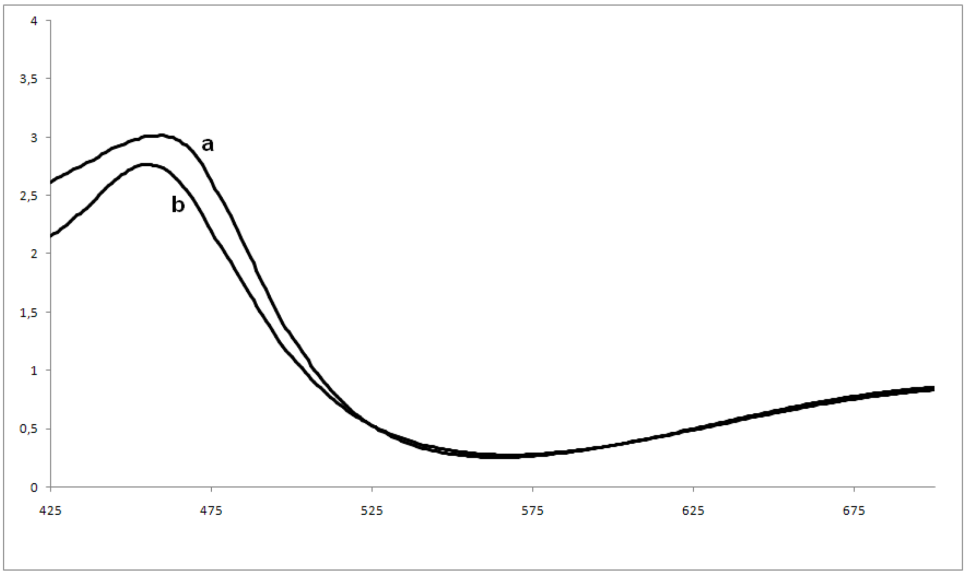


Figure S5. UV-vis spectra of **8** in THF (a) with 10 equiv of 2,4,6-collidine hydrochloride (b).

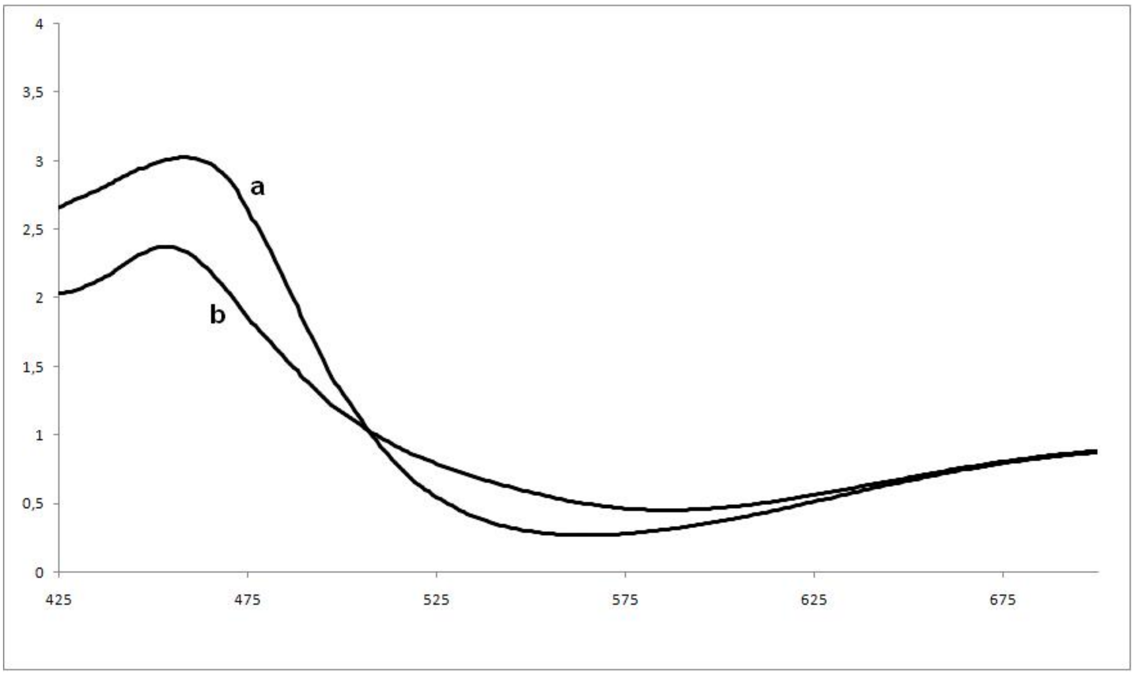


Figure S6. UV-vis spectra of **8** in THF (a) with 10 equiv of pyridine hydrochloride (b).

Control UV-vis spectrum of Figure 2.

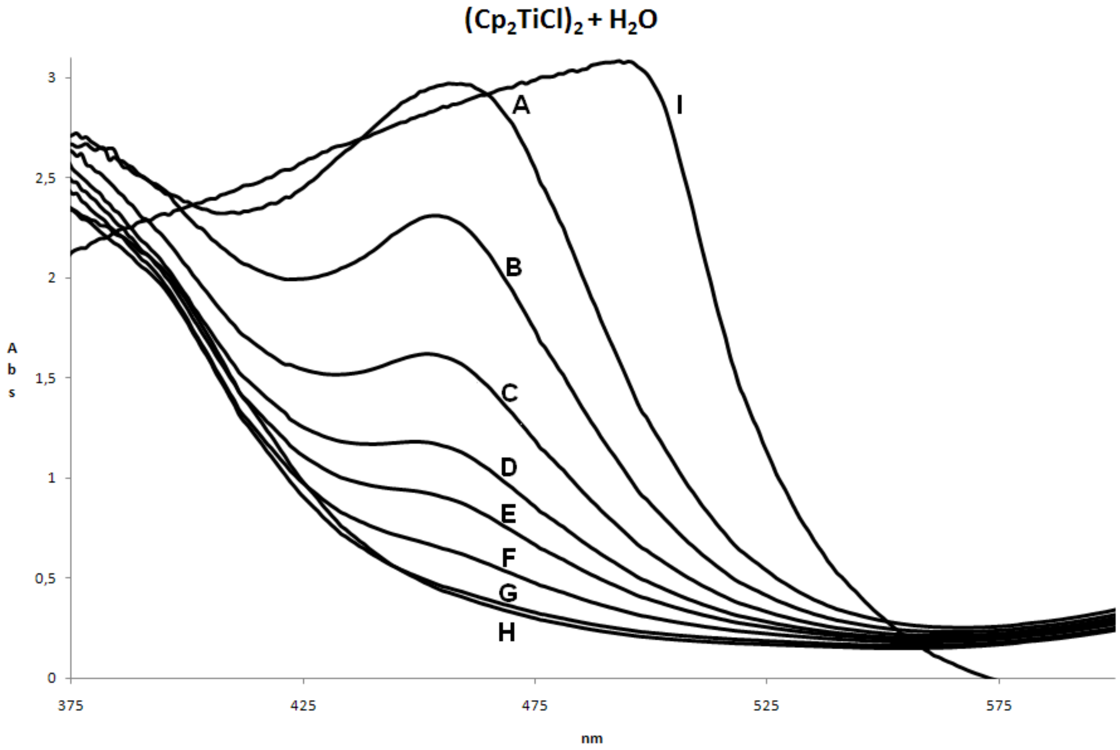


Figure S7. Absorption spectra of $(Cp_2TiCl)_2$ (0.01 M) in THF in the presence of increasing amount of water: (A) anhydrous (B) 0.5 equiv of water (C) 1 equiv of water (D) 1.5 equiv of water (E) 2 equiv of water (F) 3 equiv of water (G) 6 equiv of water (H) 8 equiv of water (I) open to air.

^{1}H NMR of compounds 8 and A in anhydrous conditions and in the presence of D_2O.

Compound 8: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.31 (s, 10H).

Compound A: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.31 (s, 10H).

Compound 8 + D_2O: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (s, 10H).

Compound A + D_2O: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (s, 10H).

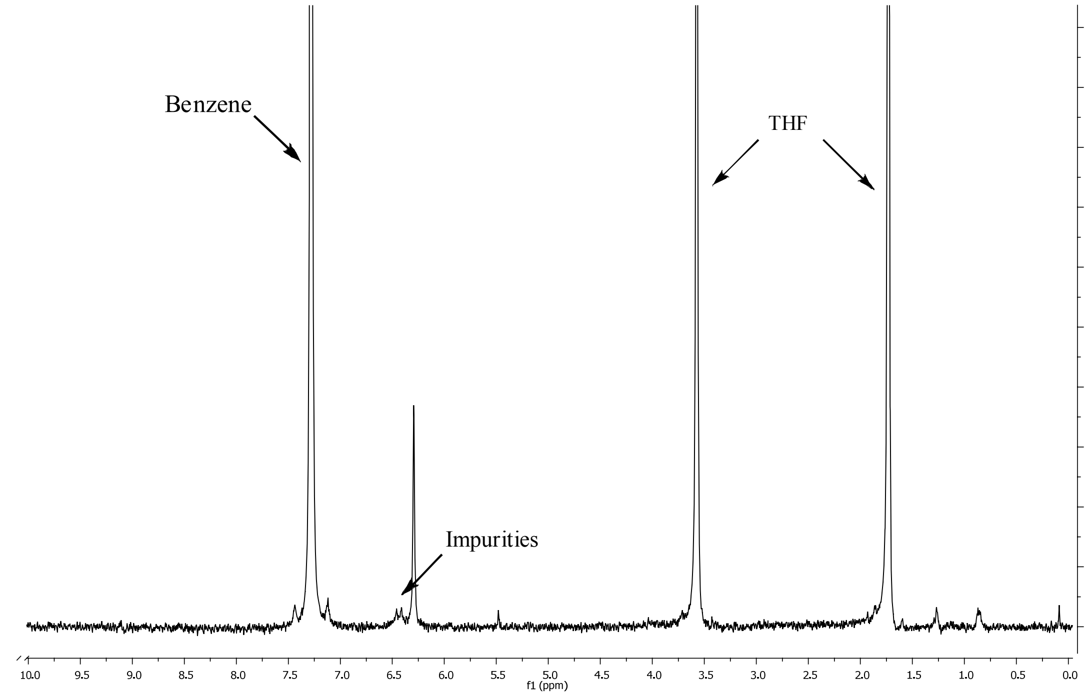
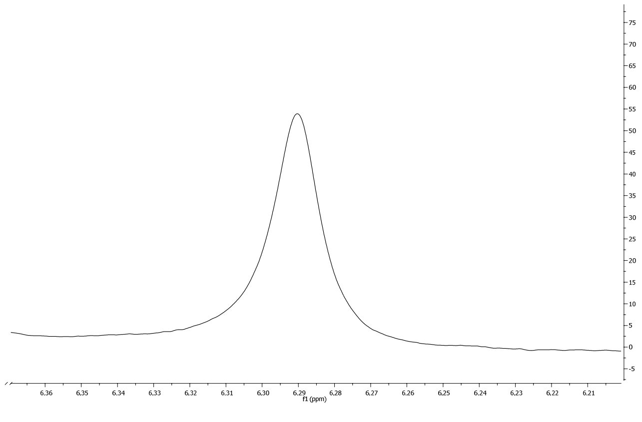
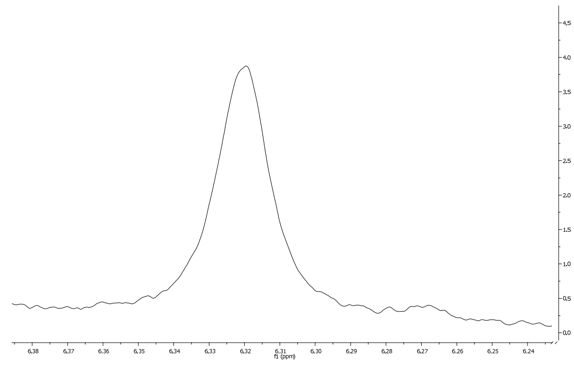


Figure S8. Copy of ^{1}H NMR of **A**[5]





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[5] In some cases we found complex signals which increased with time at 6.35-6.50 ppm. The presence of these signals was also related with a lost of the typical reactivity of Cp_2TiCl. Consequently, we assigned those signals to impurities derived from the decomposition of the oxygen sensitive Ti(III)-complexes.

Figure S9. (a) Copy of ^{1}H NMR of **8** (b) Copy of ^{1}H NMR of **A** with D_2O (4 equiv.)

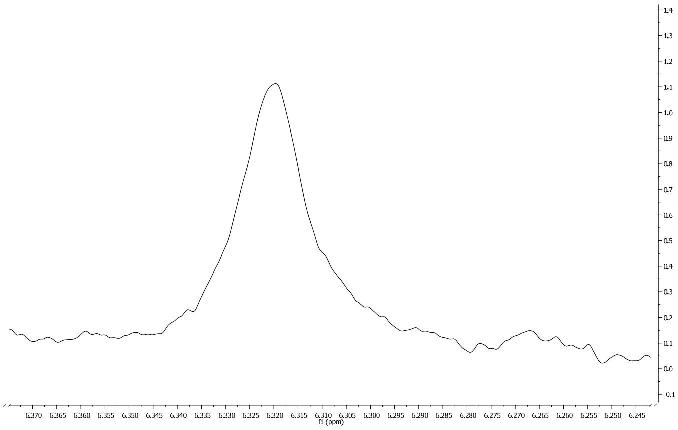
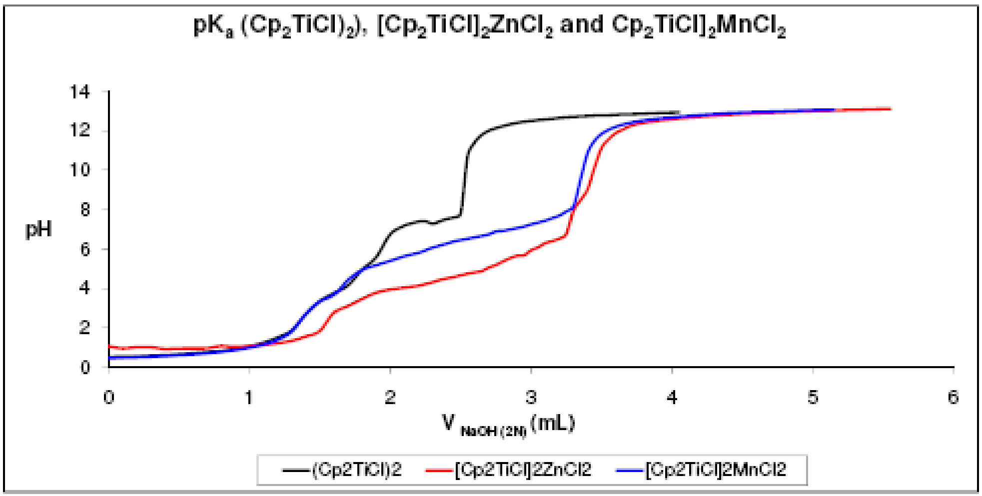


Figure S10. Copy of ^{1}H NMR of **A** with D_2O

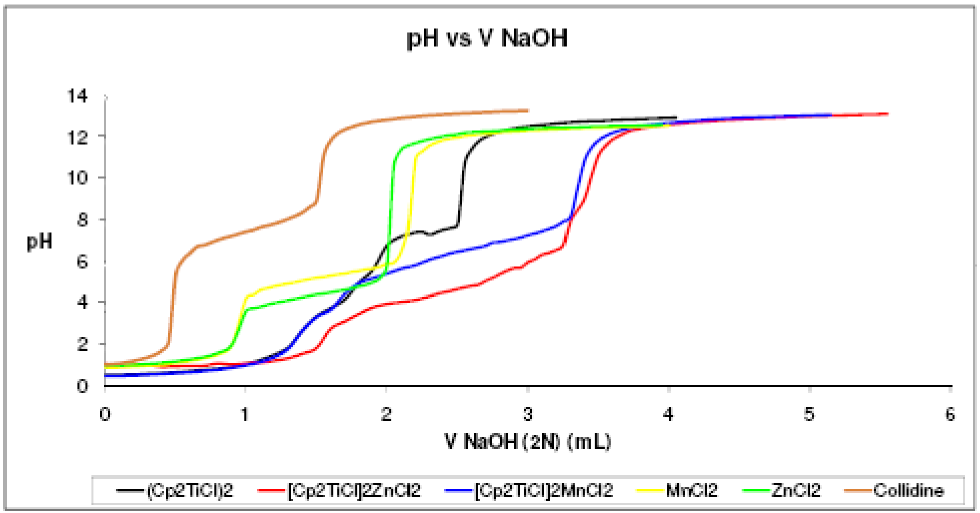
pKa Measures

pKa Values were measured using standard techniques. As experiment control we determined the pKa of 2,4,6-collidine and, within the experimental error, we obtained a similar value to the described one (pKa described =7.43, pKa measured = 7.42). The acidity of the trinuclear complexes **A** and **B** was higher than the dinuclear **8**. We attributed this fact to the presence of the potential acid species Zn^{2+} and Mn^{2+} in the sample. Therefore, we measured the apparent pKa of these cations in our conditions. Titration graphs showed that the decrease in pKa of the trinuclear complexes toward $(Cp_2TiCl)_2$ is due to the presence of such ions.



pK$_a$ ((Cp$_2$TiCl)$_2$)	7,43
pK$_a$ ([Cp$_2$TiCl]$_2$ZnCl$_2$)	5,21
pK$_a$ ([Cp$_2$TiCl]$_2$MnCl$_2$)	6,76

Figure S11. Titration graphs of aqueous solutions of complexes **9-11**.



pK$_a$ ((Cp$_2$TiCl)$_2$)	7,43	pK$_a$ (Collidine)	7,42
pK$_a$ ([Cp$_2$TiCl]$_2$ZnCl$_2$)	5,21	pK$_a$ (ZnCl$_2$)	4,36
pK$_a$ ([Cp$_2$TiCl]$_2$MnCl$_2$)	6,76	pK$_a$ (MnCl$_2$)	5,18

Figure S12. Titration graphs of aqueous solutions of complexes **8, A, B,** $MnCl_2$, $ZnCl_2$ and 2,4,6-collidine.

DOSY experiments

DOSY experiments were performed on a Varian Direct Drive 500 MHz spectrometer equipped with PERFORMA II z-axis gradient amplifier and an XHP probe with a z-axis gradient coil. Maximum gradient strength was 56 G/cm. The standard Varian pulse program, Dbppste, employing a Bipolar Pulse Pair Stimulated Echo was used. Diffusion gradient length was used with total duration of 2 ms. Gradient stabilization and diffusion delays were 0.5 ms and 50 ms, respectively. Individual rows of the quasi-2D diffusion databases were phased and baseline corrected.

Preparation of DOSY samples.

Four dry NMR tubes were introduced in a globes box under Ar atmosphere. In each tube 0.5 mmol of each compound (2 samples of $(Cp_2TiCl)_2$, and 1 sample of $[Cp_2TiCl]_2ZnCl_2{\cdot}2C_6H_6$ and $[Cp_2TiCl]_2MnCl_2{\cdot}2C_6H_6$, respectively) were introduced. Then, THF-d_8 (0.5 mL) was added. The tubes were sealed under Ar atmosphere and the samples were submitted to DOSY experiences.
After that, 0.5 mmol of Cp_2TiCl_2 was added to the sample containing $(Cp_2TiCl)_2$ complex, and, 8 mmol of D_2O were added to the other 3 samples containing $(Cp_2TiCl)_2$, $[Cp_2TiCl]_2ZnCl_2{\cdot}2C_6H_6$ and $[Cp_2TiCl]_2MnCl_2{\cdot}2C_6H_6$, respectively. These samples were submitted again to DOSY experiences. All DOSY experiences were performed the same day.

Discussion.[6]

All titanocene(III) samples are paramagnetic.[7] Therefore, a perfect and reproducible adjustment of the magnetic field was not possible. We observed in control experiments that the diffusion coefficients differ up to 1 $m^2\ seg^{-1}\ 10^{-10}$ for the same sample.
In these conditions small changes in size can not be detected. Nevertheless, the usual variation of such coefficients between closely related monomeric and dimeric structures for small molecules is expected to be higher, if Stokes-Einstein relation is fitted. In fact, differences of one order of magnitude higher have been recently reported in closely related zirconocene derivatives.[8] Therefore, similar D values for $(Cp_2TiCl)_2$ ($D = 7.87\ m^2\ seg^{-1}\ 10^{-10}$) and $(Cp_2TiCl)_2ZnCl_2$ ($D = 7.07\ m^2\ seg^{-1}\ 10^{-10}$) were related with similar size for both products. Paramagnetism of $(Cp_2TiCl)_2MnCl_2$ avoided a good quality DOSY spectra for such complex.
In order to ensure that the DOSY experiments of aquacomplex were reliable, we added 4 equiv. of D_2O to the above mentioned DOSY experiments. The registered DOSY experiments showed minor variations in the diffusion coefficients ($(Cp_2TiCl)_2$, $D = 7.70\ m^2\ seg^{-1}\ 10^{-10}$, $(Cp_2TiCl)_2ZnCl_2$, $D = 7.34\ m^2\ seg^{-1}\ 10^{-10}$) which could be attributed to small changes in the magnetic field, viscosity or density but not to a significant change in the size.[9] Therefore the new specie, assigned as aquacomplex, has similar size to the precursor complexes.

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[6] Selected referentes: D. Li, G. Kagan, R. Hopson and P. G. Williard, *J. Am. Chem. Soc.* **2009**, *131*, 5627-5634; C. S. Johnson, Jr., *Prog. NMR Spectrosc.* **1999**, *34*, 203-256; D. Li, I. Keresztes, R. Hopson and P. G. Williard, *Acc. Chem. Res.* **2009**, *42*, 270-280; T. Brand, E. J. Cabrita and S. Berger, *Prog. NMR Spectrosc.* **2005**, *46*, 159-196.

[7] Described values for the paramagnetic susceptibility of solid Ti(III) compounds is about 1.6 μB at room temperature: Ref 1; J. R. Hagadorn and J. Arnold, *Organometallics* **1998**, *17*, 1355-1368.

[8] N. E. Schlörer, E. J. Cabrita and S. Berger, *Angew. Chem. Int. Ed.* **2002**, *41*, 107-109.

[9] G. H. Sorland and D. Aksnes, *Mag. Reson. Chem.* **2002**, *40*, S139-S146.

In order to obtain information about the size of $(Cp_2TiCl)_2$ and $(Cp_2TiCl)_2ZnCl_2$, a new experiment was carried out. An equimolecular amount of commercial Cp_2TiCl_2 was added to a DOSY experience of Cp_2TiCl with a diffusion coefficient of 8.28 m^2 seg^{-1} 10^{-10} (Figure S15). A slightly shifted single signal (6.32 ppm) was observed. This fact can be attributed to a coincidence of the chemical shift of both species or to a rapid self-exchange process yielding an average signal. In any case, differences in size can be related with the presence of two different diffusion peaks or with an average value of the two diffusion coefficients. In this experiment, we obtained a single diffusion peak at D = 8.05 m^2 seg^{-1} 10^{-10} (Figure S16) which suggest that $(Cp_2TiCl)_2$ and Cp_2TiCl_2 present similar molecular size in a 0.2 M THF solution and, therefore, $(Cp_2TiCl)_2$ can be better described like the monomeric structure Cp_2TiCl.[10]

DOSY Spectra

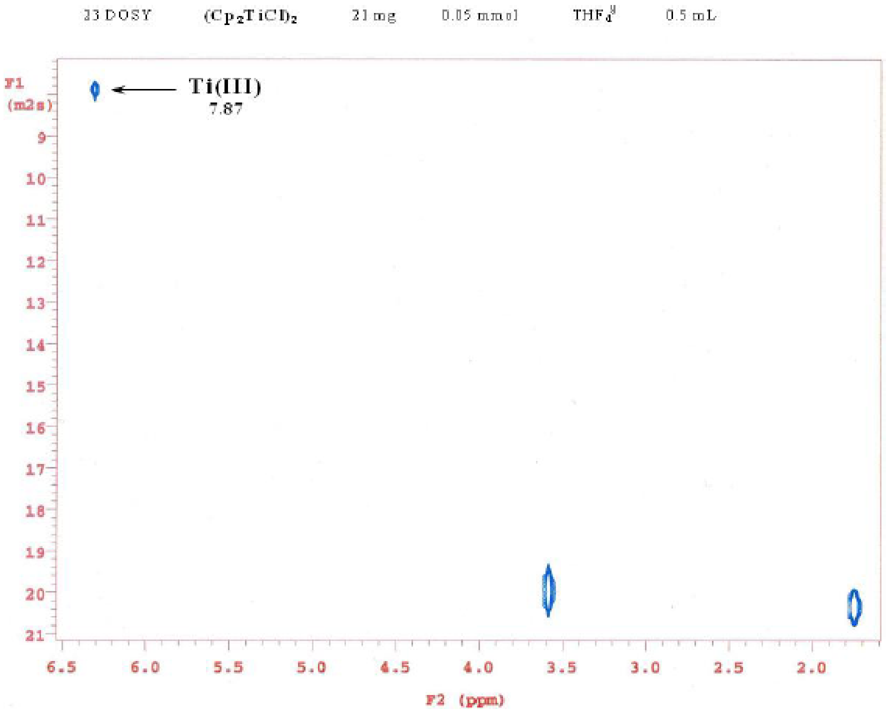

Figure S13. Copy of DOSY spectrum of $(Cp_2TiCl)_2$

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[10] More precisely, diffusion coefficients are proportional to the hydrodynamic volume, which is related to the molecular weight within similar structures.

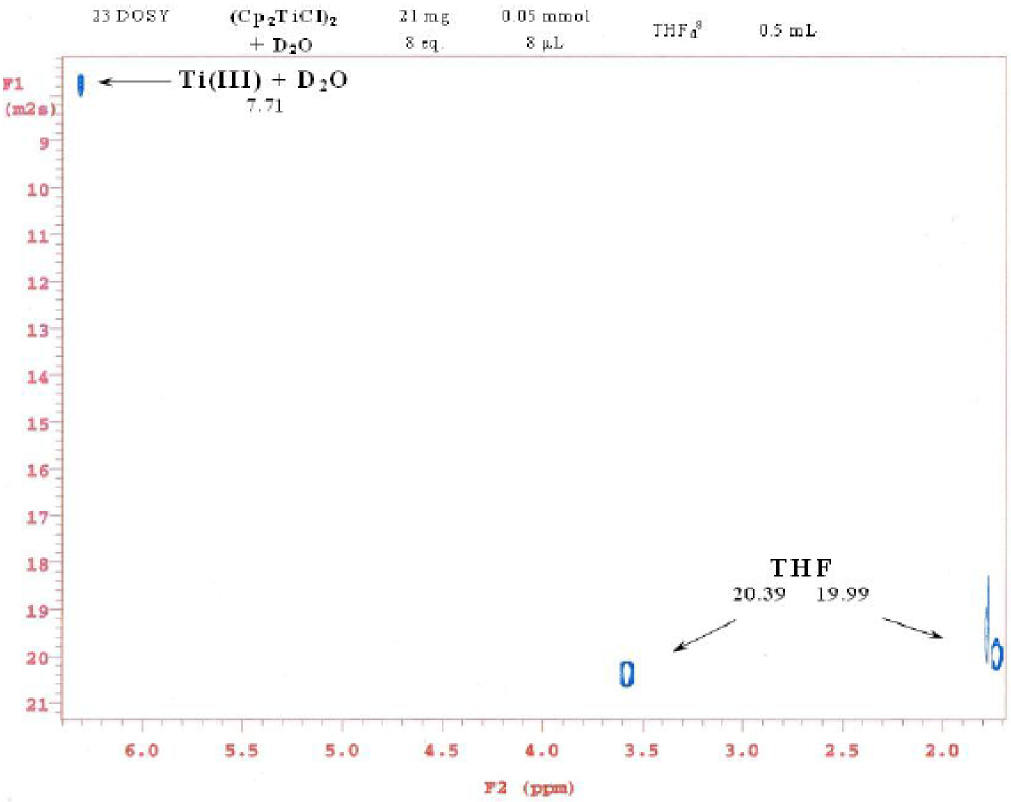

Figure S14. Copy of DOSY spectrum of $(Cp_2TiCl)_2 + H_2O$

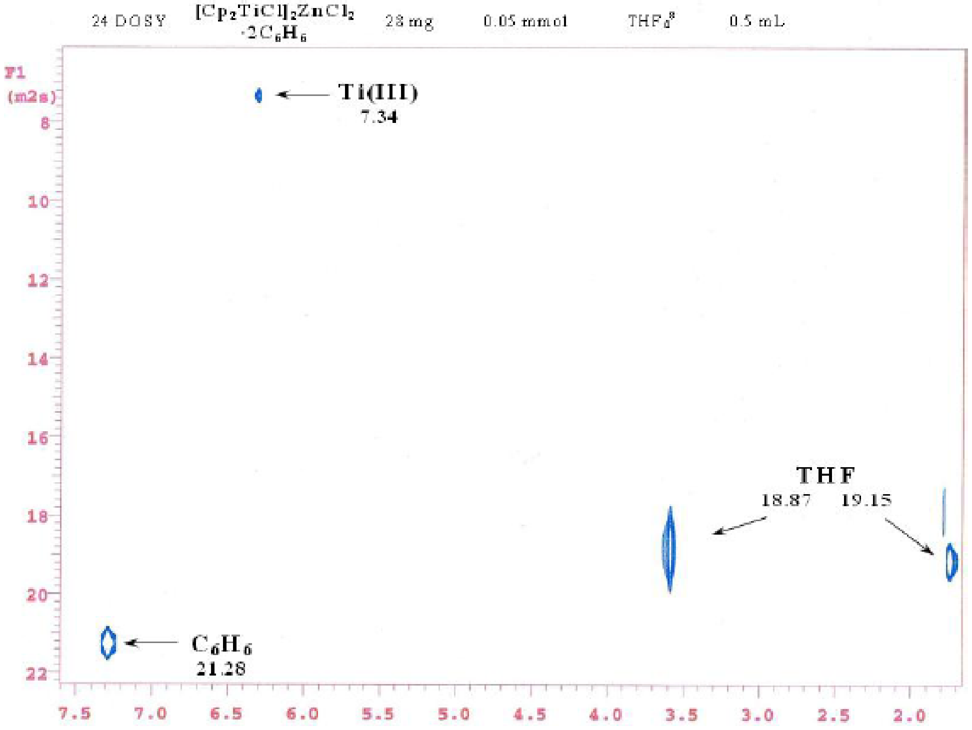

Figure S15. Copy of DOSY spectrum of $(Cp_2TiCl)_2ZnCl_2$

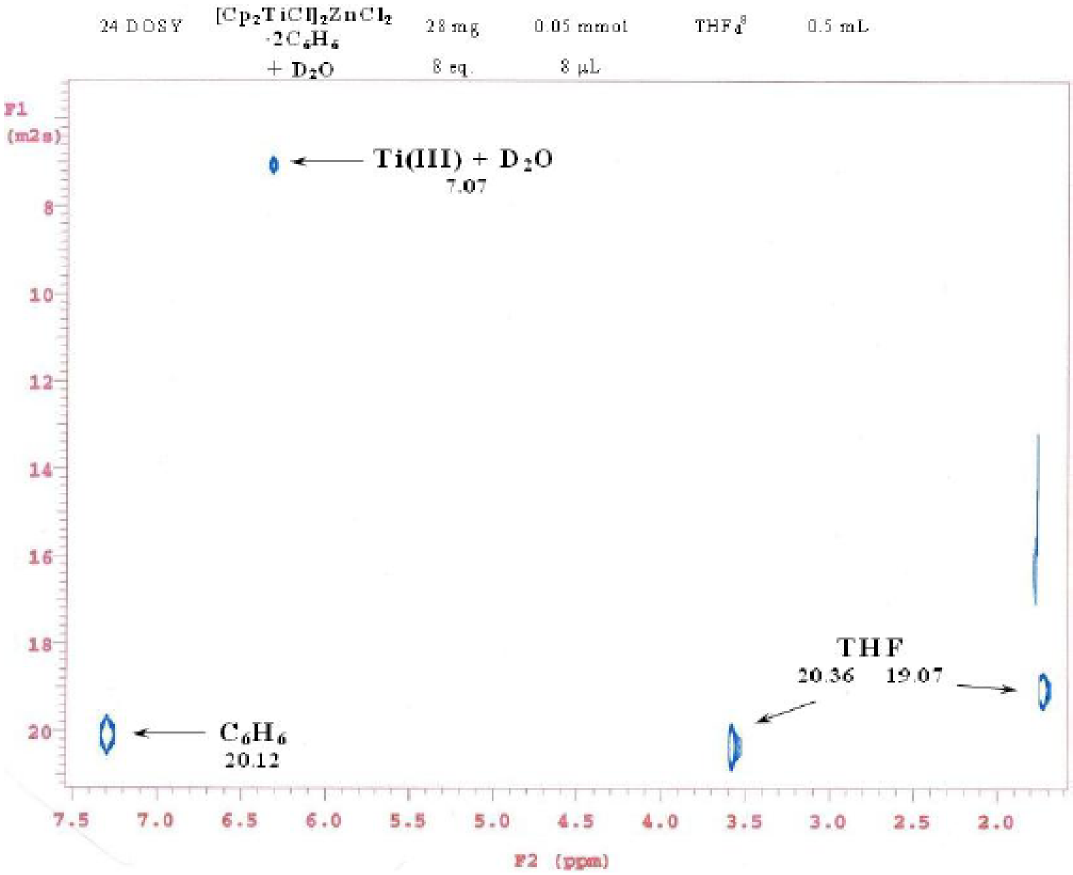

Figure S16. Copy of DOSY spectrum of $(Cp_2TiCl)_2ZnCl_2 + H_2O$

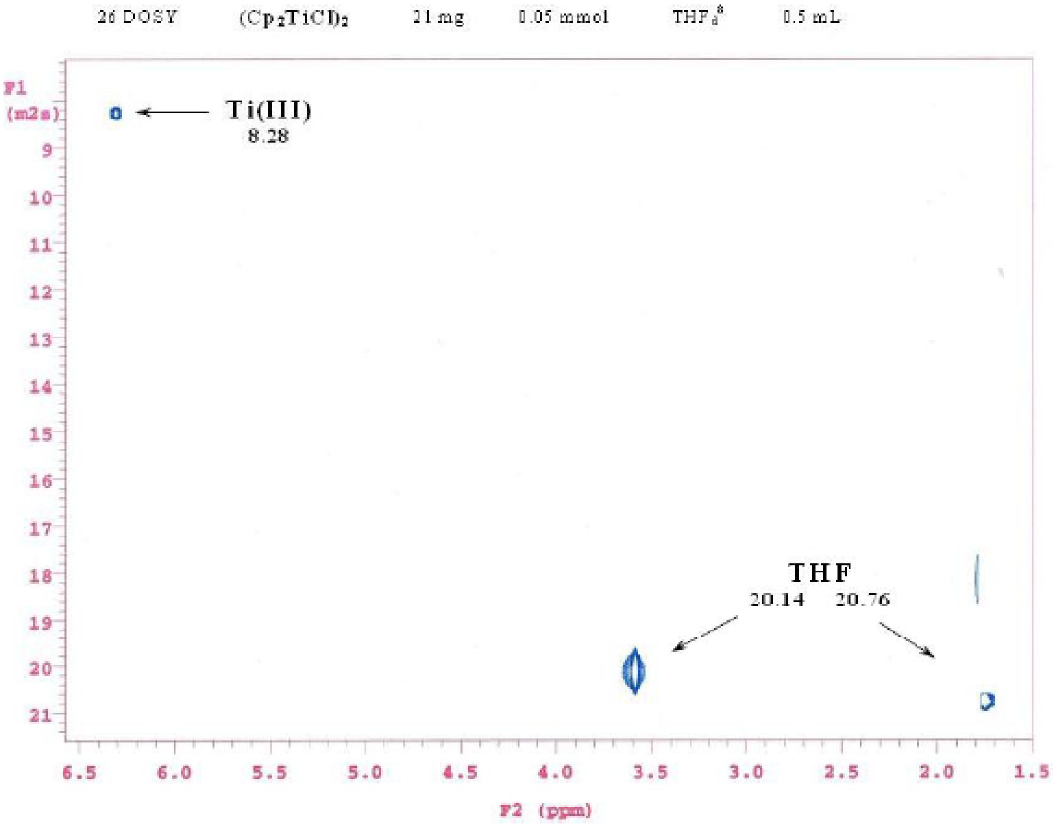

Figure S17. Copy of DOSY spectrum of $(Cp_2TiCl)_2$

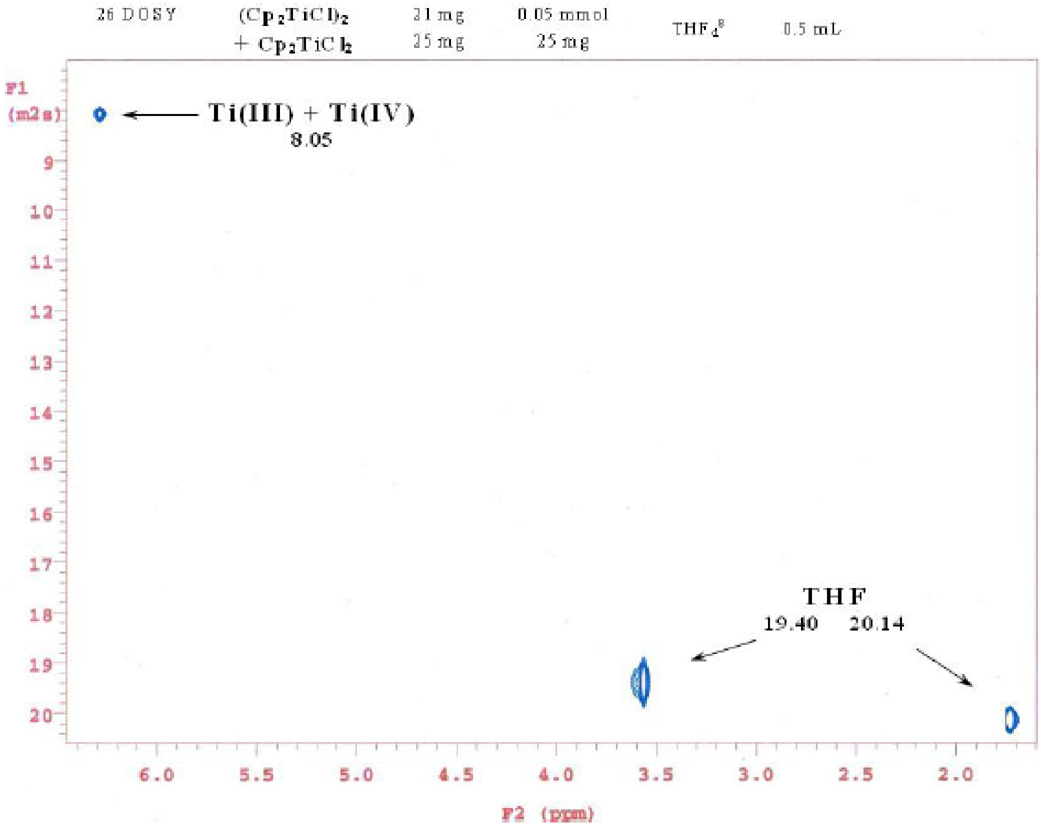

Figure S18. Copy of DOSY spectrum of $(Cp_2TiCl)_2$ and Cp_2TiCl_2

^{17}O NMR experiences.

Experimental methods. ^{17}O enriched (10% ^{17}O) water was used in all the experiments. The oxygen-17 NMR spectra were taken in a 400 MHz unit (54.219 MHz for ^{17}O). For simplicity the experiences were carried out decoupling in the ^{1}H channel.

Discussion. ^{17}O NMR can be used to obtain information about the chemical environment of the oxygen nucleus. Therefore, $^{17}OH_2$ is an excellent choice to determine if water is interacting with a Lewis acidic specie.
Initially, we determined the chemical shift of ^{17}O in mixtures of THF/water. We obtained two peaks at 18.71 and -13.89 ppm which were assigned to residual ^{17}O-tetrahydrofurane and $^{17}OH_2$ respectively.[11,12] The addition of only 4 equiv. of $^{17}OH_2$ to a solution of solid $(Cp_2TiCl)_2$ (0.05 mM in THF) promoted the disappearance of the signal corresponding to $^{17}OH_2$ whilst the ^{17}O-THF signal remain. This fact suggests a broadening of the signal due to a fast interchange of coordinated and uncoordinated water. This broadening can not be assigned to the paramagnetism of the sample because of the ^{17}O-tetrahydrofurane signal is almost unchanged. The addition of 16 equiv. of water resulted in the detection of a very broad signal between 5 and -45 ppm. The average of the chemical shift in this fast equilibrium is biased towards the uncoordinated water present in a 15:1 molar relationship. Temperature variable experiments could not be carried out due to the poor solubility of titanocene(III) complexes in THF at low temperatures.

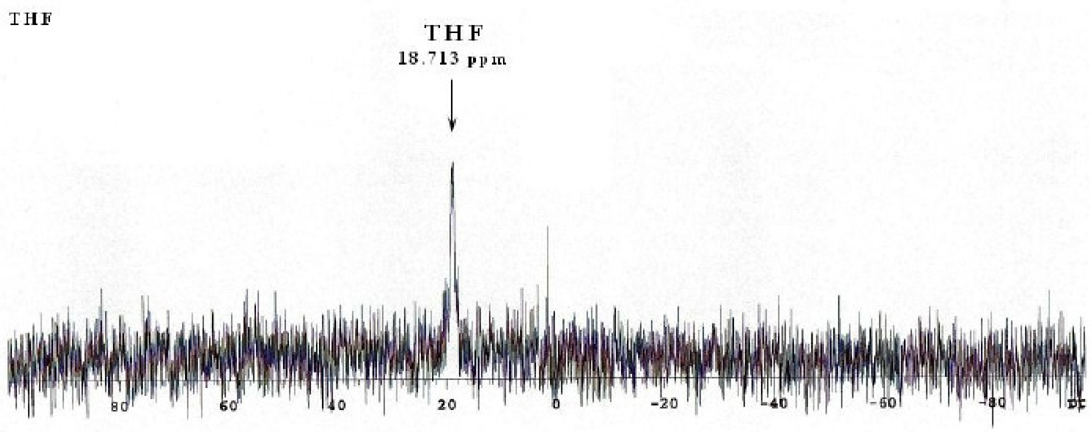

Figure S19. Copy of the ^{17}O NMR spectrum of THF

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[11] The ^{17}O chemical shift data for ^{17}O-tetrahydrofurane was not found in literature. A control experiment using only THF gave the mentioned value of 18.71 ppm.

[12] This value of -13.89 ppm is close to the reported value of $^{17}OH_2$ in THF (-15 ppm): V. Mäemets and I. Koppel, *J. Chem. Research (S)* **1994**, 480-481.

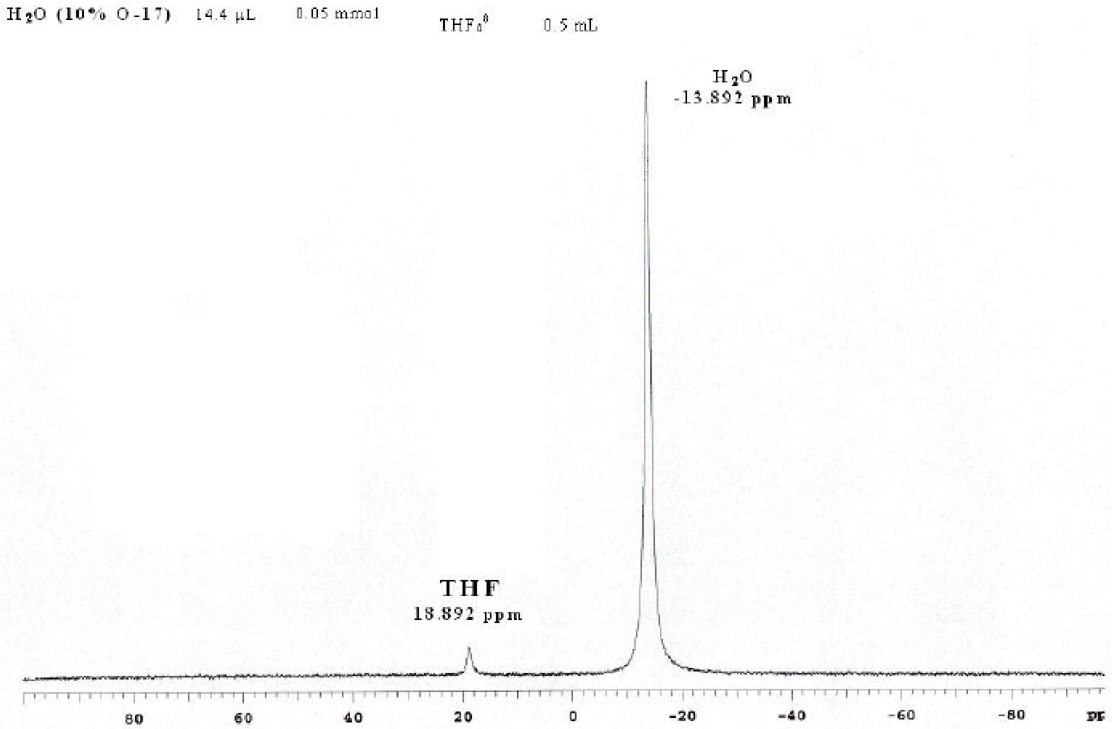

Figure S20. Copy of the ^{17}O NMR spectrum of a mixture of THF/^{17}O-water

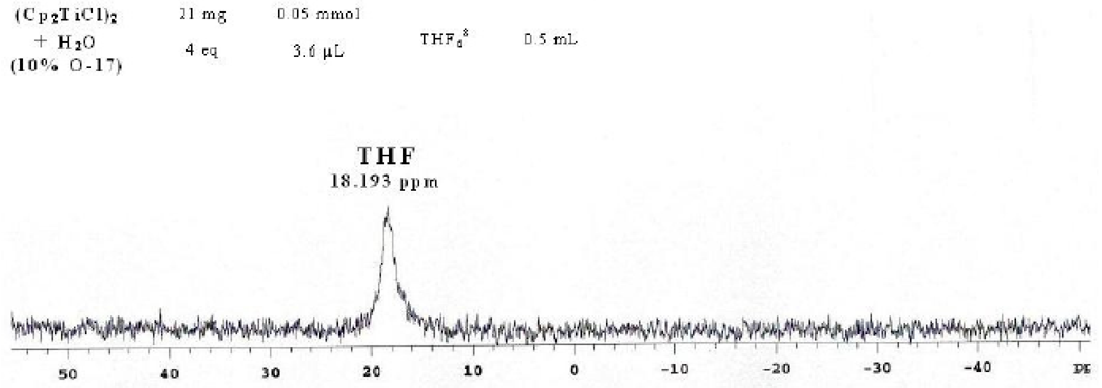

Figure S21. Copy of the ^{17}O NMR spectrum of a mixture of complex **8** and $^{17}OH_2$ (4 equiv.)

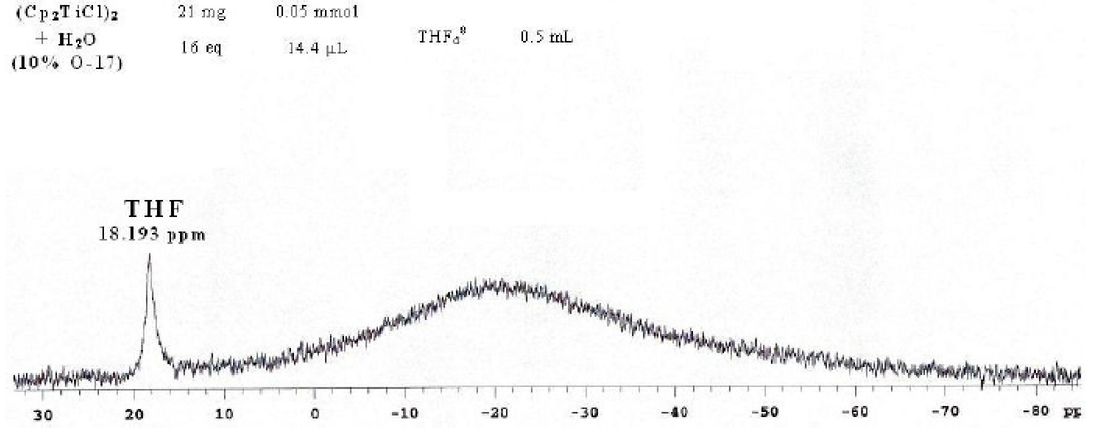

Figure S22. Copy of the ^{17}O NMR spectrum of a mixture of complex **8** and $^{17}OH_2$ (16 equiv.)

ELECTROCHEMICAL MEASUREMENTS

Apparatus

Electrochemical measurements were performed with an AUTOLAB PGSTAT30 electrochemistry system. Cyclic and square-wave voltammetry (CV and SWV, respectively) studies were carried out in a three-electrode cell under nitrogen atmosphere in anhydrous deoxygenated THF containing 0.15 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte. Polycrystalline Pt was used as working electrode; the counter electrode was a Pt gauze and the reference electrode was a silver wire quasi-reference electrode. Ferrocene (Fc) was used as internal standard, and all potentials in this work are referred to the Fc^+/Fc (abbreviation for ferrocenium/ferrocene) couple.

Procedure and results

Based on the seminal works of Skrydstrups and Daasbjerg[13] on the electrochemistry of Cp_2TiCl, we were interested in the study of the effect of H_2O in the reduction potential of Cp_2TiCl, generated in THF from Cp_2TiCl_2 and Mn dust.

As control experiment we reproduced the cyclic voltammetry of a standard solution of Cp_2TiCl (20 mM). It was prepared by stirring of a mixture of Cp_2TiCl_2 (100 mg, 0.40 mmol) and Mn dust (176 mg, 3.22 mmol) under an argon atmosphere in strictly dry THF (20 mL) until the solution turned into green (about 15 min).

In the voltammetric experiment, a THF solution of $TBAPF_6$ (20 mL, 0.15 M) was added to the electrochemical cell. The cell was closed and flushed with nitrogen for 10 min. The standard solution of Cp_2TiCl in strictly dry THF (5 mL) was added to the electrochemical cell and the solution was deoxygenated for 1 min.
At the end of the experiment a small amount of ferrocene was added, and the potential of the Fc^+/Fc couple was measured.

The CV recorded at 0.1 V/s and the SWV recorded at 15 Hz of Cp_2TiCl in THF solution in the absence of H_2O are presented in Figure S21a and S21b respectively. According to reported values, the cyclic voltammogram exhibits oxidation peaks at -0.81 V and -0.49 V vs Fc^+/Fc. On the reverse sweep a reduction peak appears at -1.28 V vs Fc^+/Fc.

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[13] R. J. Enemærke, J. Larsen, T. Skrydstrup and K. Daasbjerg, *J. Am. Chem. Soc.* **2004**, *126*, 7853-7864.

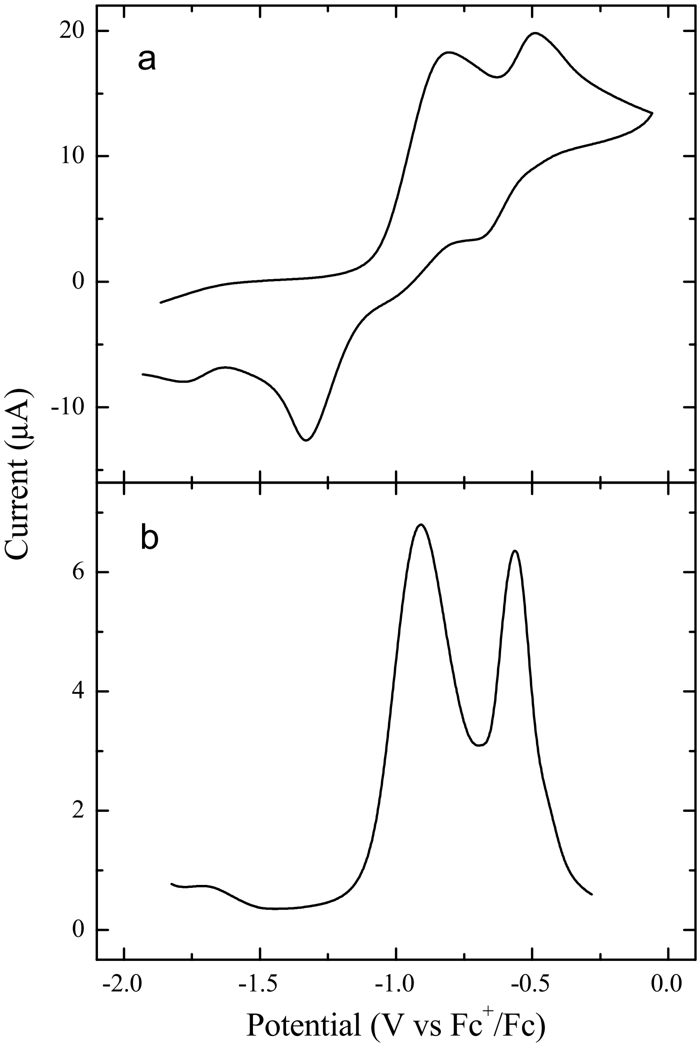


Figure S23

Subsequently, the effect of adding H_2O (10 equiv) to the solutions of Cp_2TiCl was studied. To this end, a deoxygenated solution of H_2O (73 mg, 4.02 mmol) in THF (2 mL) was added to the standard solution of Cp_2TiCl and the mixture was stirred until it turned blue (about 10 min).

In the voltammetric experiment, a THF solution of $TBAPF_6$ (22 mL, 0.15 M) was added to the electrochemical cell. The cell was closed and flushed with nitrogen for 10 min. 3 mL of the standard solution of Cp_2TiCl in aqueous THF was added to the electrochemical cell and the solution was deoxygenated for 1 min.
At the end of the experiment a small amount of ferrocene was added, and the potential of the Fc^+/Fc couple was measured.

The CV recorded at 0.1 V/s and the SWV recorded at 15 Hz of Cp_2TiCl in THF solution in the presence of H_2O (10 equiv) are presented in Figure S22a and S22b respectively. The first CV oxidation peak appears at -0.82 V vs Fc^+/Fc. The comparison of the cyclic voltammetric responses shown in Figure S21a and S22a reveals that the first oxidation peak is completely independent of the presence of water. The second oxidation wave appears at an oxidation potential that is 60 mV lower than the previously reported one. Although this change is not directly related with this work, new experiments to explain this phenomena are under way. On the reverse sweep, both voltammograms exhibit similar reduction peaks.

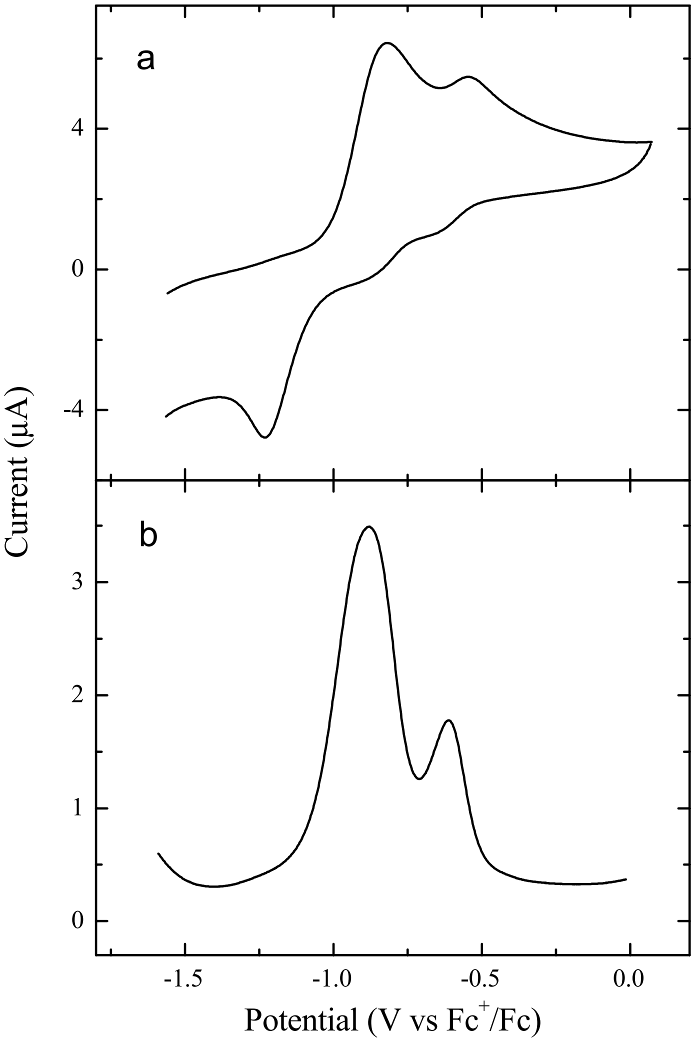
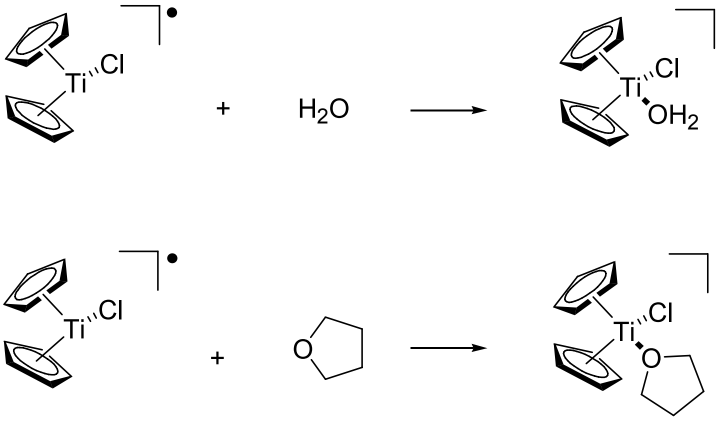


Figure S24

COMPUTATIONAL METHODS

Calculations were performed with the GAUSSIAN 03 series of programs.[14] The geometries of all complexes were optimized at the DFT level using the B3LYP hybrid functional,[15] using the standard 6-31G(d) basis set for C, H, O and Cl. The standard LANL2DZ basis set, which includes a relativistic pseudopotential, was used for Ti. Unrestricted B3LYP was used for the radical species. Transition states were graphically located. Harmonic frequencies were calculated at the same level of theory to characterize the stationary points and to determine the zero-point energies (ZPE).

Calculated reaction energy for the coordination of H_2O or THF to Cp_2TiCl



	Δ(E+ZPE) (kcal mol^{-1})	ΔG (kcal mol^{-1})
H_2O	-12.2	-0.8
THF	-4.5	+9.0

---

[14] Gaussian 03, Revision B.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam,, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, .J Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A.Pople, Gaussian, Inc., Pittsburgh PA, 2003.

[15] A.D. Becke, *Phys. Rev. A* **1988**, *38*, 3098-3100; C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789.

Calculated E+ZPE (hartrees) at B3LYP/6-31G(d) level for H_2O and THF

	E+ZPE (hartrees)	G (hartrees)
H_2O	-76.385895	-76.404206
THF	-232.328183	-232.356827

Cp_2TiCl

```
---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
---------------------------------------------------------------------
    1         22           0        0.000010    0.108507   -0.000005
    2         17           0       -0.000127    2.441369   -0.000001
    3          6           0       -2.321438    0.401138   -0.486107
    4          6           0       -2.226137    0.110761    0.898279
    5          6           0       -1.709049   -1.200462    1.038037
    6          6           0       -1.495269   -1.723316   -0.266581
    7          6           0       -1.862222   -0.728993   -1.211263
    8          1           0       -2.631671    1.345321   -0.910728
    9          1           0       -2.455837    0.796074    1.703906
   10          1           0       -1.512468   -1.713700    1.970942
   11          1           0       -1.116089   -2.708255   -0.502428
   12          1           0       -1.814906   -0.821625   -2.288953
   13          6           0        2.321413    0.401311    0.486081
   14          6           0        2.226135    0.110886   -0.898296
   15          6           0        1.709149   -1.200383   -1.038016
   16          6           0        1.495410   -1.723217    0.266615
   17          6           0        1.862285   -0.728838    1.211269
   18          1           0        2.631573    1.345529    0.910676
   19          1           0        2.455786    0.796189   -1.703946
   20          1           0        1.512605   -1.713657   -1.970909
   21          1           0        1.116301   -2.708175    0.502492
   22          1           0        1.814977   -0.821445    2.288962
---------------------------------------------------------------------
Zero-point correction=                           0.170316
(Hartree/Particle)
 Thermal correction to Energy=                    0.181692
 Thermal correction to Enthalpy=                  0.182636
 Thermal correction to Gibbs Free Energy=         0.129023
 Sum of electronic and zero-point Energies=           -905.288923
 Sum of electronic and thermal Energies=              -905.277548
 Sum of electronic and thermal Enthalpies=            -905.276603
 Sum of electronic and thermal Free Energies=         -905.330216
```

$Cp_2TiCl(OH_2)$

```
---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
---------------------------------------------------------------------
    1         22           0        0.009211   -0.005296    0.082282
    2         17           0       -0.072211    2.379758   -0.745033
    3          8           0        0.080776    1.293809    1.948538
    4          1           0       -0.746863    1.280449    2.454117
    5          1           0        0.059753    2.133089    1.425021
```

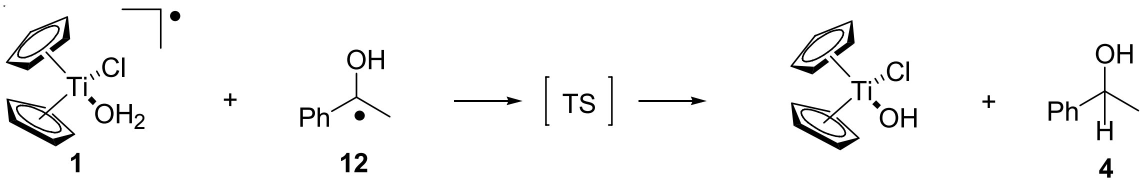
```
     6          6           0       -2.347142    0.157914    0.446013
     7          6           0       -1.902091   -1.033704    1.086519
     8          6           0       -1.448881   -1.914798    0.077997
     9          6           0       -1.619783   -1.273383   -1.182980
    10          6           0       -2.187657   -0.002823   -0.953063
    11          1           0       -2.740468    1.044358    0.927405
    12          1           0       -1.905394   -1.237159    2.150716
    13          1           0       -1.040806   -2.903908    0.236356
    14          1           0       -1.358082   -1.685647   -2.148812
    15          1           0       -2.388827    0.751486   -1.700003
    16          6           0        2.197978   -0.487001    1.008878
    17          6           0        2.342428    0.395445   -0.089873
    18          6           0        1.932994   -0.290260   -1.267602
    19          6           0        1.520717   -1.587599   -0.885058
    20          6           0        1.671138   -1.705286    0.527379
    21          1           0        2.383652   -0.240960    2.045795
    22          1           0        2.670999    1.423814   -0.044103
    23          1           0        1.911519    0.124781   -2.266293
    24          1           0        1.145168   -2.356510   -1.547487
    25          1           0        1.429862   -2.574849    1.125067
 ---------------------------------------------------------------------
Zero-point correction=                           0.195675
(Hartree/Particle)
 Thermal correction to Energy=                    0.209428
 Thermal correction to Enthalpy=                  0.210372
 Thermal correction to Gibbs Free Energy=         0.154235
 Sum of electronic and zero-point Energies=           -981.694360
 Sum of electronic and thermal Energies=              -981.680606
 Sum of electronic and thermal Enthalpies=            -981.679662
 Sum of electronic and thermal Free Energies=         -981.735800
```

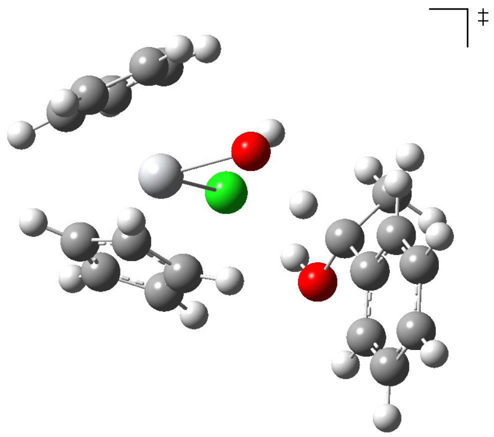
Cp$_2$TiCl(THF)

```
--------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
     1         22           0        0.702285    0.017777    0.051139
     2         17           0        0.306631   -0.139180    2.476868
     3          6           0       -3.713563    0.284012   -1.087323
     4          6           0       -2.286389   -0.226078   -1.351796
     5          6           0       -3.880821    0.138260    0.450799
     6          8           0       -1.597163   -0.084724   -0.096198
     7          6           0       -2.555225   -0.478131    0.918259
     8          1           0       -3.815147    1.329787   -1.392207
     9          1           0       -4.450310   -0.296683   -1.650198
    10          1           0       -1.736457    0.344160   -2.101506
    11          1           0       -2.285248   -1.286095   -1.642575
    12          1           0       -4.034671    1.116283    0.915782
    13          1           0       -4.730276   -0.495227    0.722151
    14          1           0       -2.601665   -1.575832    0.942855
    15          1           0       -2.174010   -0.119838    1.871059
    16          6           0        0.443377    2.348432    0.475749
    17          6           0        0.175986    2.189829   -0.907746
    18          6           0        1.361180    1.749690   -1.536217
    19          6           0        2.377557    1.668084   -0.539981
    20          6           0        1.813640    2.044303    0.697497
    21          1           0       -0.271441    2.619995    1.239379
    22          1           0       -0.779675    2.348640   -1.389678
    23          1           0        1.477535    1.515769   -2.586820
    24          1           0        3.401029    1.355846   -0.701119
    25          1           0        2.310716    2.037368    1.657255
    26          6           0        0.322929   -2.341140   -0.487208
```

```
   27          6           0        1.325971   -2.315111    0.503839
   28          6           0        2.448384   -1.628676   -0.022299
   29          6           0        2.142683   -1.262598   -1.361534
   30          6           0        0.819221   -1.682207   -1.646178
   31          1           0       -0.667311   -2.761145   -0.366487
   32          1           0        1.225360   -2.677183    1.515971
   33          1           0        3.374220   -1.430787    0.502289
   34          1           0        2.803013   -0.748737   -2.046332
   35          1           0        0.299063   -1.555589   -2.587206
 ---------------------------------------------------------------------
Zero-point correction=                           0.289879
(Hartree/Particle)
 Thermal correction to Energy=                    0.307619
 Thermal correction to Enthalpy=                  0.308563
 Thermal correction to Gibbs Free Energy=         0.241620
 Sum of electronic and zero-point Energies=          -1137.624381
 Sum of electronic and thermal Energies=             -1137.606641
 Sum of electronic and thermal Enthalpies=           -1137.605697
 Sum of electronic and thermal Free Energies=        -1137.672640
```

Calculated transition state and reaction energy for the H-atom transfer from 9 to radical 10





	kcal mol^{-1}
Δ(E+ZPE)$^{\neq}$	11.7
ΔE$^{\neq}$	11.6
ΔG$^{\neq}$	25.9

	kcal mol^{-1}
Δ(E+ZPE)	-28.3
ΔG	-26.5

12

```
---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1          6           0        0.543540    1.229995    0.000019
    2          6           0        1.967535   -1.172376   -0.000015
    3          6           0       -0.182319    0.002533   -0.000017
    4          6           0        1.930556    1.242216    0.000018
    5          6           0        2.660798    0.046034   -0.000003
    6          6           0        0.581465   -1.204005   -0.000016
    7          6           0       -1.598198   -0.046653   -0.000046
    8          6           0       -2.551518    1.103486   -0.000018
    9          8           0       -2.164466   -1.299752    0.000073
   10          1           0        0.011573    2.176283    0.000068
   11          1           0        2.520411   -2.108827   -0.000021
   12          1           0        2.453023    2.195846    0.000045
   13          1           0        3.746820    0.063581   -0.000004
   14          1           0        0.058278   -2.153336   -0.000023
   15          1           0       -3.206751    1.079957    0.885838
   16          1           0       -3.207496    1.079295   -0.885300
   17          1           0       -2.042084    2.067972   -0.000609
   18          1           0       -3.129198   -1.210139   -0.000105
 ---------------------------------------------------------------------
Zero-point correction=                           0.147839
(Hartree/Particle)
 Thermal correction to Energy=                    0.156585
 Thermal correction to Enthalpy=                  0.157529
 Thermal correction to Gibbs Free Energy=         0.112903
 Sum of electronic and zero-point Energies=           -385.295999
 Sum of electronic and thermal Energies=              -385.287252
 Sum of electronic and thermal Enthalpies=            -385.286308
 Sum of electronic and thermal Free Energies=         -385.330935
```

TS

```
---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1         22           0       -1.801201   -0.186800    0.056143
    2         17           0       -1.339478    1.762793   -1.561879
    3          8           0       -0.239764    0.746654    1.080585
    4          1           0       -0.374438    1.685322    0.845892
    5          6           0        2.046954    1.170422   -0.339938
    6          6           0        3.243052    0.355722    0.058010
    7          6           0        3.742183    0.427886    1.371607
    8          6           0        3.866552   -0.510300   -0.855853
    9          6           0        4.846051   -0.329411    1.754648
   10          6           0        4.975607   -1.262463   -0.471266
   11          6           0        5.469803   -1.175673    0.832885
   12          6           0        2.156070    2.680139   -0.063434
   13          8           0        1.669226    0.899343   -1.649599
   14          1           0        3.254687    1.070171    2.099937
   15          1           0        3.479880   -0.573340   -1.866433
   16          1           0        5.218702   -0.263080    2.773172
   17          1           0        5.456295   -1.918158   -1.192386
   18          1           0        6.332120   -1.765821    1.130977
   19          1           0        2.962731    3.102554   -0.672898
```

```
    20          1           0        1.219839    3.178191   -0.337014
    21          1           0        2.368652    2.884796    0.989670
    22          1           0        0.789169    1.323089   -1.805683
    23          1           0        1.157820    0.809568    0.352918
    24          6           0       -3.048115    1.473678    1.261772
    25          6           0       -2.782537    0.431787    2.202448
    26          6           0       -3.463112   -0.721328    1.768671
    27          6           0       -4.176453   -0.391302    0.576859
    28          6           0       -3.918242    0.963164    0.266249
    29          1           0       -2.661073    2.483092    1.298533
    30          1           0       -2.135093    0.506056    3.065441
    31          1           0       -3.446597   -1.688782    2.253032
    32          1           0       -4.801483   -1.062785    0.002746
    33          1           0       -4.278476    1.503187   -0.598029
    34          6           0       -0.033685   -1.753754   -0.526995
    35          6           0       -0.669265   -1.385258   -1.737215
    36          6           0       -2.015146   -1.822450   -1.684106
    37          6           0       -2.202310   -2.480978   -0.437088
    38          6           0       -0.983391   -2.417073    0.290327
    39          1           0        0.991599   -1.538679   -0.260879
    40          1           0       -0.215249   -0.823577   -2.539056
    41          1           0       -2.761627   -1.681774   -2.455030
    42          1           0       -3.115001   -2.953585   -0.100838
    43          1           0       -0.804695   -2.819133    1.279355
 ---------------------------------------------------------------------
Zero-point correction=                           0.343633
(Hartree/Particle)
 Thermal correction to Energy=                    0.366004
 Thermal correction to Enthalpy=                  0.366948
 Thermal correction to Gibbs Free Energy=         0.289795
 Sum of electronic and zero-point Energies=          -1366.971651
 Sum of electronic and thermal Energies=             -1366.949280
 Sum of electronic and thermal Enthalpies=           -1366.948336
 Sum of electronic and thermal Free Energies=        -1367.025488
```

Cp$_2$TiCl(OH)

```
---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
     1         22           0        0.003990    0.055320    0.228722
     2          8           0        0.088047    0.252776    2.074418
     3         17           0       -0.012283    2.374195   -0.298695
     4          1           0       -0.739305    0.535521    2.493259
     5          6           0       -2.417853    0.163613    0.472569
     6          6           0       -2.016734   -1.149945    0.819545
     7          6           0       -1.463396   -1.755942   -0.331255
     8          6           0       -1.557096   -0.822176   -1.406511
     9          6           0       -2.157121    0.351545   -0.908810
    10          1           0       -2.835965    0.908678    1.137225
    11          1           0       -2.058393   -1.595086    1.804830
    12          1           0       -1.064199   -2.759184   -0.389758
    13          1           0       -1.230942   -0.982834   -2.424922
    14          1           0       -2.323926    1.262659   -1.462847
    15          6           0        2.252210   -0.662966    0.884605
    16          6           0        2.398393    0.443258    0.028704
    17          6           0        1.911244    0.073573   -1.260380
    18          6           0        1.458319   -1.258120   -1.186621
    19          6           0        1.626699   -1.705111    0.157235
    20          1           0        2.451027   -0.668309    1.946119
    21          1           0        2.752427    1.424374    0.309852
    22          1           0        1.863058    0.720320   -2.125643
```

```
    23          1           0        1.035503   -1.833180   -1.998641
    24          1           0        1.359377   -2.678689    0.546643
 ---------------------------------------------------------------------
 Zero-point correction=                           0.184905
 (Hartree/Particle)
  Thermal correction to Energy=                    0.197771
  Thermal correction to Enthalpy=                  0.198716
  Thermal correction to Gibbs Free Energy=         0.145377
  Sum of electronic and zero-point Energies=           -981.115351
  Sum of electronic and thermal Energies=              -981.102484
  Sum of electronic and thermal Enthalpies=            -981.101540
  Sum of electronic and thermal Free Energies=         -981.154879
```

1-Phenyletanol (4)

```
 ---------------------------------------------------------------------
  Center     Atomic     Atomic              Coordinates (Angstroms)
  Number     Number      Type              X           Y           Z
  ---------------------------------------------------------------------
     1          6           0        0.709346   -1.229189   -0.350887
     2          6           0        1.778394    1.252580    0.327144
     3          6           0       -0.151013   -0.142722   -0.151702
     4          6           0        2.089899   -1.081792   -0.205994
     5          6           0        2.628467    0.161235    0.133392
     6          6           0        0.398132    1.101286    0.186254
     7          6           0       -1.658846   -0.314026   -0.273821
     8          6           0       -2.319756   -0.599064    1.075908
     9          8           0       -2.294568    0.858030   -0.785122
    10          1           0        0.295041   -2.197693   -0.624993
    11          1           0        2.191104    2.223979    0.587642
    12          1           0        2.744736   -1.934479   -0.366248
    13          1           0        3.703401    0.279577    0.241259
    14          1           0       -0.266936    1.948222    0.329206
    15          1           0       -1.855319   -1.168235   -0.943576
    16          1           0       -2.128457    0.225458    1.770600
    17          1           0       -3.402223   -0.702570    0.946923
    18          1           0       -1.924103   -1.521520    1.512822
    19          1           0       -1.848430    1.093172   -1.614429
  ---------------------------------------------------------------------
 Zero-point correction=                           0.161902
 (Hartree/Particle)
  Thermal correction to Energy=                    0.170181
  Thermal correction to Enthalpy=                  0.171125
  Thermal correction to Gibbs Free Energy=         0.128784
  Sum of electronic and zero-point Energies=           -385.920160
  Sum of electronic and thermal Energies=              -385.911882
  Sum of electronic and thermal Enthalpies=            -385.910937
  Sum of electronic and thermal Free Energies=         -385.953279
```