Computational studies of the unusual water adduct \([\text{Cp}_2\text{TiMe(OH}_2\text{)]}^+\)†: the roles of the solvent and the counterion†

Jörg Saßmannshausen

The recently reported cationic titanocene complex \([\text{Cp}_2\text{TiMe(OH}_2\text{)]}^+\) was subjected to detailed computational studies using density functional theory (DFT). The calculated NMR spectra revealed the importance of including the anion and the solvent (CD$_2$Cl$_2$) in order to calculate spectra which were in good agreement with the experimental data. Specifically, two organic solvent molecules were required to coordinate to the two hydrogens of the bound OH$_2$ in order to achieve such agreement. Further elaboration of the role of the solvent led to Bader’s QTAIM and natural bond order calculations. The zirconocene complex \([\text{Cp}_2\text{ZrMe(OH}_2\text{)]}^+\) was simulated for comparison.

Introduction

Group 4 metallocenes have been the workhorse for a number of reactions for some decades now. In particular the cationic compounds \([\text{Cp}_2\text{MR}]^+\) (M = Ti, Zr, Hf; R = Me, CH$_2$Ph) are believed to be the active catalysts for a number of polymerization reactions such as Kaminsky type α-olefin,$^1$–$^{10}$ carboxationic$^{11}$–$^{15}$ or ring-opening lactide polymerization.$^{16}$–$^{18}$ For these highly electrophilic cationic compounds, water is usually considered a poison as it leads to catalyst decomposition. In this respect it was quite surprising that Baird recently reported the characterisation of the complex \([\text{Cp}_2\text{TiMe(OH}_2\text{)]}[\text{B(C}_6\text{F}_5\text{)}_4]\) (I) using NMR spectroscopy.$^{19}$ For some years now, we have been interested in the use of molecular modelling as a tool to predict NMR spectra and the use of NMR spectroscopy for confirming our theoretical results.$^{20}$–$^{27}$ For this reason, we modelled a number of possible compounds which are summarised in Chart 1 and compared these theoretical chemical shifts with the ones observed by Baird. The proposed compound \([\text{Cp}_2\text{TiMe(OH}_2\text{)]}^+\) (1) together with the outer sphere ion pair \([\text{Cp}_2\text{TiMe(OH}_2\text{)]}[\text{MeB(C}_6\text{F}_5\text{)}_3]\) (2) served as the starting point for our investigations. Furthermore, the solvent adducts \([\text{Cp}_2\text{TiMe(OH}_2\text{)](CH}_2\text{Cl}_2}\) (3) and \([\text{Cp}_2\text{TiMe(OH}_2\text{)](CH}_2\text{Cl}_2}\) (4), and for comparison, the zirconocene compounds \([\text{Cp}_2\text{ZrMe(OH}_2\text{)]}^+\) (5), \([\text{Cp}_2\text{ZrMe(OH}_2\text{)]CH}_2\text{Cl}_2}\) (6) and \([\text{Cp}_2\text{ZrMe(OH}_2\text{)](CH}_2\text{Cl}_2}\) (7) were also modelled.

Chart 1

Model compounds used for the calculation of the chemical shifts.

In order to gain insight into the ‘acidity’ of the OH$_2$ protons we calculated the pK$_a$ of 1, 3, 5 and 6. These models are summarised in Chart 2.

Improved reliability of the pK$_a$ data was achieved by employing the MP2 level of theory in calculations of certain species which are denoted by the suffix MP2.

To gain some insight into the ground state energy differences between the ‘naked’ cation \([\text{Cp}_2\text{TiMe}]^+\) (III) and the solvent adduct \([\text{Cp}_2\text{TiMe(CH}_2\text{Cl}_2}]\) (13) as well as between \([\text{Cp}_2\text{TiMe(CH}_2\text{Cl}_2}]\) [H$_2$O] (14) and 3, these compounds have been modelled too (cf. Chart 3).

The methyl borate anion \([\text{MeB(C}_6\text{F}_5\text{)}_3]\) was used instead of the borate \([\text{B(C}_6\text{F}_5\text{)}_4]\) in the calculations in order to save computational cost.

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The $pK_a$ calculations were performed using the PCM-SMD model as implemented in the program, with water as the solvent of choice. These calculations were done at the B3LYP/ECP11 level and additionally at the MP2/ECP11 level of theory. For the MP2 computation, GAMESS 2012, R2 was used. Here the B3LYP geometry was used as the starting point for the calculations at the MP2/ECP11 level of theory. We basically followed a procedure published in ref. 35. For the proton, an experimentally obtained Gibbs free energy value of $-6.28$ kcal mol$^{-1}$ for the gas phase and $-264.61$ kcal mol$^{-1}$ for the hydration was employed.

Tables of Cartesian coordinates of all calculated structures are available as ESI$^+$ in $x$, $y$, $z$ format. QTAIM$^{36}$ and NBO analyses$^{37}$ were performed using the DZVP$^{38}$ all-electron basis set on Ti and Zr and 6-311G(d,p) for C, H, F, and B, denoted DZVP1. Diagrams of the electron charge density plots were obtained using AIM2000.$^{39,40}$ MOLDEN was used for the chemical representation of the calculated compounds.$^{41}$

### Results and discussion

#### Structural and NMR results

In order to verify our computational approach, we calculated the well-known structure of dimethyl titanocene (II) and the cationic methyl titanocene [Cp$_2$TiMe]$^+$ (III). For II, we computed a Ti–Me bond distance of 2.16 Å at the B3LYP/ECP11 level and a Me–Ti–Me angle of 91.7° which fits well with the experimentally observed values$^{42}$ of 2.170(2) and 2.180(2) Å, and 91.3(1)$^o$. Thus, we can be confident that our chosen level of theory is appropriate here.

For the methyl group in III we observe two expected Ti–C–H angles of 120.8° and 121.3° with the third one rather acute (84.3°). These metric parameters and the reduced $J_{	ext{CH}}$ coupling constant of 93.8 Hz, compared with the remaining two coupling constants of approximately 142 Hz, clearly indicate an agostic interaction here.$^{43,44}$ While Bader analysis very clearly shows an absence of such a bonding path between the Ti and the C–H bond.$^{45}$ This is, however, not unexpected as Lein pointed out recently.$^{51}$ Indeed, detailed NBO analysis supports the $\alpha$-agostic interaction in III (see Table 2 and ESI$^+$ for a plot of the electron density and NBO).

The starting geometry of the water adduct I was constructed by adding one molecule of water to III. Selected metric parameters, chemical shifts and CH coupling constants of III, I, 3 and 4 are summarised in Table 1.

As is evident from Table 1, upon coordination of one molecule of water to III the rather acute Ti–C–H1 angle relaxes to around 114°, concomitant with a small elongation of the Ti–C bond and a more significant change of the $J_{	ext{CH}}$ coupling constant. Addition of one or two molecules of dichloromethane does not substantially change the steric parameters of the methyl group.

A more dominant change upon dichloromethane coordination can be observed in the calculated proton and carbon NMR spectra. For the solvate free cation I we calculate $\delta$(OCH$_3$)
2.79 ppm, which is in stark contrast with the experimentally observed value of 4.77 ppm. However, addition of one or two molecules of CH2Cl2 improves the situation significantly, with 5.10/2.98 ppm (3, one molecule of CH2Cl2) and 5.03/4.93 ppm (4, two molecules of CH2Cl2) which is in excellent agreement with the experimental data. For comparison, for the outer sphere ion pair (OSIP)53 the calculated average chemical shift of $\delta$(OH$_2$) = 6.42 ppm. These findings very clearly indicate that the solvent adduct 4 is in fact the observed compound in the NMR. Similar findings have been reported before, most notably the coordination of dichloromethane to cationic zirconocene benzyl compounds.25

### $pK_a$ computational results

One of the real advantages of molecular modelling is the possibility to investigate molecules which are, under normal experimental conditions, difficult to observe. This could be because these molecules of interest are either of fleeting existence or require special conditions like high pressure or simply would not exist as such in reality. With this in mind we were interested in knowing whether the above findings are mirrored in the ‘acidity’ of the coordinated water and thus we calculated the $pK_a$ values of compounds 1, 3, 5 and 6 (cf. Table 2). We do not claim that the calculated numbers are the ones which would be experimentally observed, as to the best of our knowledge to date there is no reliable method to compute the $pK_a$ without the use of a known base54 or the inclusion of the first solvation shell beyond the immediate ligand sphere.55 Thus, whilst we are confident that the computed numbers are reasonable they must be regarded as approximations.

For 1, the calculated $pK_a$ of 4.57 at the MP2/ECP11 level of theory (6.29 for B3LYP/ECP11) is somewhat higher than that for the solvent adduct 3 (MP2: 2.80; B3LYP: 5.19). For comparison, the first $pK_a$ of the dicaticonic titanocene bis-water adduct [Cp$_2$Ti(OH)$_2$)$_2$$^+$ (IV) was measured to be $\sim$3.51 as reported by Marks.56 For the zirconium congener 5 the calculated $pK_a$ of 2.99 (MP2) and 8.65 (B3LYP) is again somewhat higher than that for the solvent adduct 6 (MP2: 1.21; B3LYP: 7.27). Three observations can be made: (i) addition of one molecule of CH2Cl2 lowers the $pK_a$, (ii) the zirconium congener is more acidic than the titanium compounds at the MP2/ecp11 level of theory, and (iii) the computed $pK_a$ values at the B3LYP level of

### Table 1

Selected bond distances, angles, chemical shifts and CH coupling constants of III, 1, 3 and 4. Bond distances are in Å, angles in °, chemical shifts in ppm relative to TMS and coupling constants in Hz. Values in parentheses are at the MP2/ECP11 level of theory.

| Compound | d(Ti–C) | d(Ti–H1) | d(Ti–H2) | d(Ti–H3) | d(Ti–H4) | d(Ti–H5) |
|----------|---------|----------|----------|----------|----------|----------|
| III      | 2.08(2.09) | 1.12(1.14) | 1.09(1.09) | 1.09(1.09) | 2.15(2.14) | 0.96(0.97) |
| 1        | 2.15(2.19) | 1.09(1.10) | 1.09(1.10) | 1.09(1.10) | 2.13(2.11) | 0.96(0.96) |
| 3        | 2.15(2.20) | 1.09(1.10) | 1.09(1.10) | 1.09(1.10) | 2.13(2.11) | 0.97(0.97) |
| 4        | 2.15(2.20) | 1.09(1.10) | 1.09(1.10) | 1.09(1.10) | 2.13(2.11) | 0.97(0.97) |

| Compound | δ(CH$_3$) | J(CH$_3$) | J(CH$_3$) | J(CH$_3$) | δ(OH$_2$) |
|----------|-----------|-----------|-----------|-----------|-----------|
| III      | 122.8     | 93.8      | 141.7     | 141.9     | 125.8     |
| 1        | 166.6     | 131.5     | 126.5     | 126.5     | 128.2     |
| 3        | 2.79      | 128.3     | 128.8     | 128.8     | 118.8     |
| 4        | 6.29      | 6.37      | 6.29      | 6.29      | 6.29      |

| Compound | δ(C$_x$H$_y$) | δ(C$_x$H$_y$) | δ(C$_x$H$_y$) |
|----------|--------------|--------------|--------------|
| III      | 117.8        | 117.8        | 117.8        |
| 1        | 131.4        | 131.4        | 131.4        |
| 3        | 126.7        | 126.7        | 126.7        |
| 4        | 6.29         | 6.29         | 6.29         |
Electronic structural analysis: Bader and NBO

In order to gain a better insight into the electronic structure of the computed compounds III, 1, 3, 4, 5, and 6, we performed Bader’s QTAIM and natural bond orbital analysis. We were particularly interested in the change of the O-H bond properties upon coordinating to the cationic metal centre and upon addition of one or two molecules of CH₂Cl₂. The results are summarised in Table 3.

It is clear from Table 3 that addition of one or two molecules of CH₂Cl₂ changes the electronic properties of the metal–oxygen and oxygen–hydrogen bonds. These changes are in line with the calculated chemical shifts. For example, the Ti–O electron density at the bond critical point (bcp) increases from $\rho(r) = 0.0536$ to $\rho(r) = 0.0576$ ($\rho(r) = 0.0593$ for two CH₂Cl₂) upon addition of one molecule CH₂Cl₂. There is a concomitant change of the O–H bond parameters. Upon addition of one CH₂Cl₂ the electron density of the coordinated H decreases to $\rho(r) = 0.3451$ from $\rho(r) = 0.3580$ whereas for the non-coordinated hydrogen it increases to $\rho(r) = 0.3591$. This observation is further reinforced by the (Natural) charges: upon addition of one CH₂Cl₂ the originally evenly charged hydrogens acquire a small charge imbalance: 0.515 for the ‘free’ hydrogen and 0.518 for the coordinate hydrogen. Thus, electron density is removed from the hydrogens upon coordination of even one molecule of CH₂Cl₂ and this electron density is pulled towards the more electronegative oxygen (change of (Natural) charge from $-0.907$ to $-0.927$). This change in the electronic properties of these hydrogens is further reflected in the change of the calculated chemical shifts: for the ‘free’ hydrogen we find a shift of $\delta(1H) = 2.98$ ppm and for the coordinated hydrogen a shift of $\delta(1H) = 5.10$ ppm. The addition of a second CH₂Cl₂ removes this small change in the electronic properties of the hydrogens.

Ground state energy calculations

In light of the different compounds already calculated, it is reasonable to look into the ground state energy between the naked cation III and its solvent adduct [Cp₂TiMe(CH₂Cl₂)]⁺ (10). To save computational time and also to eliminate the

| B3LYP/ecp11 | MP2/ecp11 |
|-------------|-----------|
| 6.29        | 4.57      |
| 5.19        | 2.80      |
| 8.65        | 2.99      |
| 7.27        | 1.21      |

Table 2 Summary of the calculation of $pK_a$ of 1, 3, 5 and 6

Here, at the B3LYP/ecp11 level of theory we obtain an energy difference of $+9.2$ kJ mol⁻¹ (MP2/ecp11: $+15.4$ kJ mol⁻¹), clearly indicating that the reaction is more on the left hand side, i.e. 1 is more stable than 5 which is in accord with the $pK_a$ predictions made before.

With respect to the addition of one molecule of CH₂Cl₂, the calculated chemical shifts are a useful probe. The calculated chemical shift of the non-coordinated HO-H is 2.98 ppm whereas for the coordinated hydrogen it is 5.10 (Table 1). Thus, the coordinated hydrogen is deshielded, thus rendering it more positive, which in turn means that it should be easier to ionize. We will look into the bond properties in more detail in the next section. Compared with titanium the atomic radius of zirconium is larger (calculated radius for Zr: 206 pm; Ti: 176 pm); thus there is less steric congestion around the metal which leads to a tighter binding of the water to the cationic metalloocene. As a result of the reduced congestion the zirconium compounds are stronger Lewis acids in general, which is mirrored here by a lower $pK_a$ value and, more generally, by a higher activity in, for example, $\alpha$-olefin polymerization.
need to search for a global minimum, we calculated CH₂Cl₂ at
the B3LYP/6-311G(d,p) level of theory and added the electronic
energies of that and III together. As expected, the ‘solvated’
cation 13 is around 323 kJ mol⁻¹ lower in energy than the
naked cation 3. Addition of one molecule of water to 13, which
was optimized as 14, results in the formation of the water
adduct 3 which is around 80 kJ mol⁻¹ lower in energy than 14.
Similar results can be obtained for the equilibrium between
the Zr compounds [Cp₂ZrMe(CH₂Cl₂)]⁺[H₂O] (15) and 6. Here
we obtain a value of around 88 kJ mol⁻¹.

Conclusions
From the reported calculations it is clear that, in solution, the
cationic titanocene water adduct [Cp₂TiMe(OH₂)]⁺ (1) does not
exist as such two molecules of the solvent CH₂Cl₂ are co-
ordinated to the water by means of hydrogen bonding. Thus,
the observed chemical shifts very clearly indicate that at least two
molecules of the solvent CH₂Cl₂ are co-
ordinated to the water by means of hydrogen bonding. Thus,
the observed chemical shifts actually belong to this solvated
species, [(Cp₂TiMe(OH₂)][CH₂Cl₂)]⁺ (4), and as such represent
the outer sphere ion pair [(Cp₂TiMe(OH₂)][CH₂Cl₂)]⁺[B(C₆F₅)]⁻.

The trends of our calculated chemical shifts are mirrored in the
QTAIM model and the computed pKₐ values. As expected, the
zirconium derivatives show a similar behaviour and are
more acidic than the titanium ones. It would be interesting to
determine whether these acidic protons could be utilised, for
example in the carbocationic polymerization of isobutene.

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