Computational studies of the unusual water adduct [Cp₂TiMe(OH₂)]⁺: the roles of the solvent and the counterion†

Jörg Saßmannshausen

The recently reported cationic titanocene complex [Cp₂TiMe(OH₂)]⁺ 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 (CD₂Cl₂) 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 OH₂ 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 [Cp₂ZrMe(OH₂)]⁺ 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 [Cp₂MR]⁺ (M = Ti, Zr; R = Me, CH₂Ph) are believed to be the active catalysts for a number of polymerization reactions such as Kaminsky type α-olefin,1–10 carbocationic11–15 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 [Cp₂TiMe(OH₂)][B(C₆F₅)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 [Cp₂TiMe(OH₂)]²⁺ (1) together with the outer sphere ion pair [Cp₂TiMe(OH₂)][MeB(C₆F₅)₃]⁻ (2) served as the starting point for our investigations. Furthermore, the solvent adducts [[Cp₂TiMe(OH₂)][CH₂Cl₂]]⁺ (3) and [[Cp₂TiMe(OH₂)][CH₂Cl₂]]⁻ (4), and for comparison, the zirconocene compounds [Cp₂ZrMe(OH₂)]²⁺ (5), [[Cp₂ZrMe(OH₂)][CH₂Cl₂]]⁺ (6) and [[Cp₂ZrMe(OH₂)][CH₂Cl₂]]⁻ (7) were also modelled.

In order to gain insight into the ‘acidity’ of the OH₂ protons we calculated the pKₐ of 1, 3, 5 and 6. These models are summarised in Chart 2.

Improved reliability of the pKₐ 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 [Cp₂TiMe]⁺ (II) and the solvent adduct [Cp₂TiMe(CH₂Cl₂)]⁺ (13) as well as between [Cp₂TiMe(CH₂Cl₂)]⁺ [H₂O] (14) and 3, these compounds have been modelled too (cf. Chart 3).

The methyl borate anion [MeB(C₆F₅)₃]⁻ was used instead of the borate [B(C₆F₅)₄] in the calculations in order to save computational cost.

Chart 1

Model compounds used for the calculation of the chemical shifts.

Chart 2

Model compounds used for the calculation of the acidities of the OH₂ protons.
The pKₐ 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/ECPI1 level and additionally at the MP2/ECPI1 level of theory. For the MP2 computation, GAMESS 2012, R2 was used.³⁴ Here the B3LYP geometry was used as the starting point for the calculations at the MP2/ECPI1 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. QTAIM⁶ and NBO analyses³⁷ were performed using the DZVP¹⁸ 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.¹¹

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 [C₆H₅TiMe]⁺ (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 values⁴² of 2.170(2) and 2.180(2) Å, and 91.3(1)°. 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 ¹JCH 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.⁴⁵,⁵¹ This is, however, not unexpected as Lein pointed out recently.⁵² Indeed, detailed NBO analysis supports the α-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 ¹JCH 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 ²δ(OH₂)
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 we calculated an average chemical shift of δ(OH₂) = 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

**pKₐ 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 pKₐ 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 pKₐ without the use of a known base24 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 pKₐ 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 pKₐ of the dicaticionic titanocene bis-water adduct [Cp₂Ti(OH₂)]₂⁺ (IV) was measured to be ~3.51 as reported by Marks.56 For the zirconium congener 5 the calculated pKₐ of 2.99 (MP2) and 8.65 (B3LYP) is again somewhat higher than that for the solvent adduct 6 (MP2: 2.12; B3LYP: 7.28). Three observations can be made: (i) addition of one molecule of CH₂Cl₂ lowers the pKₐ; (ii) the zirconium congener is more acidic than the titanium compounds at the MP2/ecp11 level of theory, and (iii) the computed pKₐ 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
theory appear to be rather high. For example, our calculated $pK_a$ values for 1 are closer to the observed value for IV at the MP2/ecp11 level of theory. Furthermore, the $pK_a$ of tris(allyl) amine (TAA) was determined to be 8.31. It is very difficult to believe that a cationic zirconocene compound has a similar $pK_a$ as TAA. Thus, we can conclude that the obtained figures at the B3LYP level of theory are probably incorrect. It is very difficult to establish the reason for this discrepancy, especially as the computed structures are very similar.

Another way to study the relative stability of the titanium and zirconium water adducts is to look at the isodesmic reaction between the water adducts and their corresponding bases:

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 CH$_2$Cl$_2$, 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 metalloscene. 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.

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 CH$_2$Cl$_2$. The results are summarised in Table 3.

It is clear from Table 3 that addition of one or two molecules of CH$_2$Cl$_2$ 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 CH$_2$Cl$_2$) upon addition of one molecule CH$_2$Cl$_2$. There is a concomitant change of the O–H bond parameters. Upon addition of one CH$_2$Cl$_2$ 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 CH$_2$Cl$_2$ 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 CH$_2$Cl$_2$ 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 CH$_2$Cl$_2$ removes this small variation for the hydrogens and the calculated electronic parameters are again similar; however, the (Natural) charge for the oxygen has further decreased to $-0.939$. It should be noted that the Bader charges appear to be less sensitive to this and that these changes are small for the hydrogen atoms but more dominant for the oxygen. Similar observations can be made for the Zr analogue: the addition of one solvent molecule changes the electron density of the O–H bond from $\rho = 0.3565$ to $\rho = 0.3547$ (‘free’) and $\rho = 0.3288$ (coordinated) (see Table S15 in the ESI†).

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 [Cp$_2$TiMe(CH$_2$Cl)$_2$]$^+$ (10). To save computational time and also to eliminate the
Selected bond critical points (bcp) and Bader/Natural charges for 1, 3, 13, 14, and 6. Natural charges are given in parentheses. The units of electron density $\rho$ are atomic units (a.u.)

<table>
<thead>
<tr>
<th>bcp1</th>
<th>bcp2</th>
<th>bcp3</th>
<th>bcp4</th>
</tr>
</thead>
<tbody>
<tr>
<td>M=Ti or Zr</td>
<td>Non-coordinated HfCHCl$_3$</td>
<td>is present.</td>
<td>*Bond critical point between O and H (not shown on the plots).</td>
</tr>
</tbody>
</table>

From the reported calculations it is clear that, in solution, the cationic titanocene water adduct $[\text{Cp}_2\text{TiMe(OH$_2$)}]^+$ (1) does not exist as such. Our calculated chemical shifts very clearly indicate that at least two molecules of the solvent CH$_2$Cl$_2$ are coordinated to the water by means of hydrogen bonding. Thus, the observed chemical shifts actually belong to this solvated species, $[[\text{Cp}_2\text{TiMe(OH$_2$)}][\text{CH}_2\text{Cl}_2]]^+$ (4), and as such represent the outer sphere ion pair $[[\text{Cp}_2\text{TiMe(OH$_2$)}][\text{CH}_2\text{Cl}_2]]^+\text{[Cp}_2\text{F}_2\text{]}_n$. The trends of our calculated chemical shifts are mirrored in the QTAIM model and the computed $pK_a$ 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.

Conclusions

References


J.S. would like to thank Alexandra Simperler from the NSCCS/UK for useful discussions and help with the $pK_a$ calculations.