Chapter 3 Hemilabile *ansa*-Cp-arene coordination and its relevance to catalysis

From computational studies, it appears that efficient ethylene trimerisation catalysis by Cp-arene titanium complexes hinges on the careful choice of an appropriately strong metal-arene interaction, that allows stabilisation of (transient) coordinatively unsaturated species, while at the same time allowing displacement of the arene by an incoming ethylene molecule. Ligand systems that are able to adapt their coordination mode (e.g., denticity or hapticity) to the electronic or steric demands of the metal centre are designated as *hemilabile*. Most hemilabile ligands are multidentates that feature one pendant Lewis base moiety that is less strongly binding than the others, and that can readily and reversibly dissociate. Well-known examples are phosphine ligands that contain additional labile donors, such as O- or N-based functionalities.1-5 A recent study by Chomitz and Arnold on the coordination chemistry of a monoanionic [N₂P₂] ligand to transition metal dinitrogen complexes illustrates the ability of a hemilabile ligand to meet the demands of metals with different oxidation states or coordination geometries (A, Chart 3.1).6 Hemilabile ligands in which the substitutionally labile part is an arene moiety are less common, but a few examples are known and studies on arene exchange in transition metal complexes have been reported (B, Chart 3.1).7-9

Chart 3.1

Given the importance of arene coordination in titanium catalysed ethylene trimerisation, this chapter describes the experimental determination of the strength of the metal-arene interaction in *ansa*-Cp-arene titanium complexes and how this affects the catalysis. These results are supported by a computational study.
3.1. Determination of Activation Parameters for Arene Exchange

Having established the ansa-Cp-arene binding motif in cationic complexes 3a-c and 3f in the solid state (Scheme 3.1 and Chapter 2), we set out to determine the strength of arene binding in this type of compounds in solution. Slippage or dissociation of the arene is proposed for the rate-determining step in ethylene trimerisation catalysed by these complexes,\textsuperscript{10-12} and therefore a better understanding of the factors that govern the Ti-arene interaction is important for improving their performance in catalysis.

![Scheme 3.1. Synthesis of cationic ansa-Cp-arene complexes of titanium(IV); solid state structure of the cation 3f (right).](image)

Variable-temperature \(^1\)H NMR studies on compound 3f (prepared \textit{in situ} from 2f and [PhNM\textsubscript{2}H][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] in C\textsubscript{6}D\textsubscript{5}Br) showed that, due to the asymmetry induced by the SiMe\textsubscript{3} substituent, the resonances of the Me substituents on the coordinated arene moiety are inequivalent at low temperature (< 0 °C, slow exchange regime), but broaden and ultimately coalesce upon warming to ~ 40 °C (Figure 3.1). Determination of the coalescence temperature allows extraction of \(\Delta G^\ddagger\) for the process exchanging the two arene environments in 3f (Scheme 3.2).\textsuperscript{13} Although the resonances of the m-Me groups of the arene moiety are clearly inequivalent at temperatures below 0 °C, the separation is not sufficient to obtain resolved crosspeaks in the 2D NMR spectrum. As a result, attempts to extract the enthalpic and entropic contribution to the observed free energy of activation by variable temperature EXSY NMR spectroscopy were not successful. Similarly, accurate lineshape analysis is hampered by the proximity of the resonances of the exchanging groups.
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Figure 3.1. $^1$H NMR spectrum of 3f (generated *in situ* from 2f/[PhNMe$_2$H][B(C$_6$F$_5$)$_4$] in C$_6$D$_5$Br at -25 °C), with the inset showing the coalescence of the ArMe resonances upon warming (-25 → 40 °C). Resonances marked with an asterisk are for PhNMe$_2$.

Scheme 3.2. Schematic representation of arene exchange in *ansa*-Cp-arene titanium cations.

Encouraged by the stability of the cation 3f at relatively high temperatures (at least for the time required to collect the $^1$H NMR spectra), a series of complexes with a SiMe$_3$ substituent on the cyclopentadienyl part of the Cp-arene ligand was prepared (3d-3h, Scheme 3.1). These allow us to study the influence of (i) the electron-density in the pendant arene moiety and (ii) the nature of the bridging unit on the strength of the Ti-arene interaction. The cations were prepared on NMR scale as described in Chapter 2, and kept cold until inserted into the pre-cooled probe of the NMR spectrometer. For compounds 3e-3h, two distinct signals for the two sets of arene ortho- and/or meta-substituents are observed at -30 °C. Variable-temperature $^1$H NMR spectroscopy was performed to determine the coalescence temperature for arene exchange, which allows a determination of the free
energy of activation for the dynamic process.\textsuperscript{13} It is presently unclear whether transient coordination of the anion or the solvent is involved in this process. If this is the case, it is expected to affect the various derivatives in a comparable way. Data for the activation energy for arene exchange in 3d-h are collected in Table 3.1. The cation 3d, with a C\textsubscript{1} bridge and unsubstituted arene moiety showed time-averaged ¹H NMR resonances at -30 °C in C\textsubscript{6}D\textsubscript{5}Br. The same result was obtained at -60 °C (the lowest temperature that could be reached), using CD\textsubscript{2}Cl\textsubscript{2} as a solvent, suggesting that the exchange is too fast on the NMR timescale to determine the activation energy for this system.

Table 3.1. Coalescence temperature and corresponding activation energy (ΔG\textsuperscript{‡}\textsubscript{Tc}) for site exchange in 3d-3h.

<table>
<thead>
<tr>
<th>cation\textsuperscript{a}</th>
<th>arene</th>
<th>bridge</th>
<th>T\textsubscript{c} (°C)</th>
<th>ΔG\textsuperscript{‡}\textsubscript{Tc} (kJ·mol\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d</td>
<td>Ph</td>
<td>CMe\textsubscript{2}</td>
<td>&lt; -60\textsuperscript{b}</td>
<td>&lt; 45</td>
</tr>
<tr>
<td>3e</td>
<td>3,5-Me\textsubscript{2}Ph</td>
<td>CH\textsubscript{2}</td>
<td>-13.0</td>
<td>54.3(3)</td>
</tr>
<tr>
<td>3e\textsuperscript{b}</td>
<td>3,5-Me\textsubscript{2}Ph</td>
<td>CH\textsubscript{2}</td>
<td>-3.0</td>
<td>57.1(4)</td>
</tr>
<tr>
<td>3f</td>
<td>3,5-Me\textsubscript{2}Ph</td>
<td>CMe\textsubscript{2}</td>
<td>36.5</td>
<td>67.0(6)</td>
</tr>
<tr>
<td>3g</td>
<td>Ph</td>
<td>CH\textsubscript{2}CMe\textsubscript{2}</td>
<td>&gt; 80</td>
<td>74(1)\textsuperscript{c}</td>
</tr>
<tr>
<td>3h</td>
<td>3,5-Me\textsubscript{2}Ph</td>
<td>CH\textsubscript{2}CMe\textsubscript{2}</td>
<td>&gt; 100</td>
<td>&gt; 81</td>
</tr>
</tbody>
</table>

\textsuperscript{a} generated in C\textsubscript{6}D\textsubscript{5}Br from 2d-2h and [PhC][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4} at -30 °C, unless mentioned otherwise.\textsuperscript{b} in CD\textsubscript{2}Cl\textsubscript{2}.\textsuperscript{c} determined by 2D EXSY NMR spectroscopy.

From a comparison of compounds 3d and 3f it is evident that there is a significant influence of the electron-density in the arene moiety. The slow exchange regime for 3d could not be reached (down to -60 °C in CD\textsubscript{2}Cl\textsubscript{2} no sign of decoalescence is observed). Although it could be that the ¹H NMR resonances for the ortho- and meta-CH groups of the phenyl rings in 3d are accidentally overlapped, the observation of equivalent ¹³C NMR resonances suggests that the exchange is fast at all temperatures we examined. From this, an upper limit for ΔG\textsuperscript{‡}\textsubscript{Tc} of 45 kJ·mol\textsuperscript{-1} can be estimated, assuming the chemical shift difference in the slow exchange regime to be the same as found for 3f (14 Hz). Addition of two electron-donating methyl substituents in the 3- and 5-positions of the phenyl ring (3f), and keeping the bridging group the same, increases the barrier for site exchange with at least 22 kJ·mol\textsuperscript{-1} to ΔG\textsuperscript{‡}\textsubscript{Tc} = 67.0(6) kJ·mol\textsuperscript{-1} for 3f.\textsuperscript{14} This is supported by the increase in ΔG\textsuperscript{‡}\textsubscript{Tc} of 3h compared to 3g.

Changing the nature of the bridge from CMe\textsubscript{2} (3f) to CH\textsubscript{2} (3e) results in a weaker Ti-arene interaction (ΔG\textsuperscript{‡}\textsubscript{Tc} = 54.3(3) kJ·mol\textsuperscript{-1} at -13.0 °C). The stronger metal-arene interaction for 3f is most likely the result of a smaller Cp(C\textsubscript{ipso})-Cbridge-Ar(C\textsubscript{ipso}) angle compared to 3e, due to increased steric interactions of the methyl substituents on the bridging carbon atom (Thorpe-Ingold effect).\textsuperscript{15} The activation barrier for arene exchange in
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3e was shown to be slightly solvent-dependent, with $\Delta G^\ddagger_{Tc} = 57.1(4)$ kJ·mol$^{-1}$ at -3.0 ºC in CD$_2$Cl$_2$. Additionally, coalescence of the TiMe resonances was observed at +3 ºC in CD$_2$Cl$_2$ ($\Delta G^\ddagger_{Tc} = 59.5(5)$ kJ·mol$^{-1}$). The exchange of the TiMe groups can only occur by inversion at the metal centre, a process for which the arene moiety needs to be completely detached. There apparently is only a modest additional barrier of 2.4 kJ·mol$^{-1}$ to inversion. In the complexes with a C$_1$ bridge linking the cyclopentadienyl and arene rings (3d-f) the observed arene exchange indicates hemilabile behaviour of the ansa-Cp-arene ligand.

Changing the bridge length to C$_2$ (3g and 3h) leads to complexes in which the Ti-arene interaction is sufficiently strong to prevent exchange on the NMR timescale, up to temperatures where decomposition occurs rapidly (80 and 100 ºC, respectively). For 3g, the ortho-H resonances of the pendant phenyl group are sufficiently separated to allow determination of the activation parameters by 2D EXSY NMR spectroscopy. Unfortunately, its limited stability at temperatures where exchange is conveniently monitored allowed us to obtain rate data only at a single temperature. Analysis of the EXSY spectra (at 18.4 ºC with 4 different mixing times) results in $\Delta G^\ddagger = 74(1)$ kJ·mol$^{-1}$. This value, together with the estimated lower limit for exchange in 3h ($\Delta G^\ddagger_{Tc} > 81$ kJ·mol$^{-1}$) indicates that there is a considerable increase in arene binding strength in comparison to the complexes with a C$_1$ bridge.

The experimental trends described here are in accord with a recent computational study on the influence of modifications in the electron-donating ability of the pendant arene group on the ethylene oligomerisation characteristics of related zirconium/hafnium catalyst systems. Specifically, the calculated transition state energies for ethylene uptake (which requires (partial) slippage of the pendant arene moiety) increase by 13.8 and 20.9 kJ·mol$^{-1}$ on going from Ar = Ph to Ar = 3,5-Me$_2$Ph in the Cp-arene zirconium metalacycles [Ar-Z-\(\eta^5\)-C$_5$H$_5$]Zr(CH$_2$)$_n$ for Z = CMe$_2$ and CH$_2$CMe$_2$, respectively. For the cationic d$^0$ zirconium arene adducts Cp$^*$ZrMe$_2(\eta^6$-arene) (arene = benzene, toluene), exchange between coordinated and free arene was not observed by spin saturation experiments at -50 ºC in the presence of excess arene. At higher temperatures (0 ºC), the complex with a benzene ligand did show evidence for arene exchange, while this was not the case for the toluene analogue. From these data it was concluded that the substitution of a hydrogen (in benzene) by an electron-releasing methyl group (in toluene) results in stronger arene-metal bonding, but quantitative data are lacking. In a similar study, Hayes and Piers have prepared cationic d$^0$ scandium complexes supported by $\beta$-diketiminate ligands that form adducts with arenes, and arene exchange in these compounds was studied. Like in many d$^n$ ($n \neq 0$) transition metal arene complexes, the exchange was shown to proceed via a rate-limiting slippage to a lower hapticity arene coordination. The exchange data presented here for ansa-Cp-arene titanium(IV) cations are overall in good agreement with the trends that are anticipated based on literature data. Taken together with the X-ray crystal structures of 3b and 3e (Chapter 2), these results conclusively show that the longer C$_2$ bridge allows strong ansa-(\(\eta^5\)-cyclopentadienyl,\(\eta^6\)-arene) coordination, while the C$_1$ bridge results in ‘constrained geometry’ complexes approaching ansa-(\(\eta^5\)-cyclopentadienyl,\(\eta^5\)-arene) coordination with relatively low barriers for dissociation of the arene.
3.2. CATALYTIC ETHYLENE TRIMERISATION

Calculations on the catalytic cycle for ethylene trimerisation using the cationic Cp-arene titanium system suggest that rate-limiting insertion of ethylene into a five-membered metalacycle involves a certain degree of dissociation of the pendant arene moiety (Scheme 3.3).\textsuperscript{10-12} Related zirconium/hafnium systems have been calculated (although with experimental studies lacking it is not entirely clear that these may indeed enter the redox cycle that is proposed for titanium-catalysed ethylene trimerisation), and the barriers for crucial steps in the catalytic cycle were shown to be very sensitive to the donor-ability of the coordinated arene group.\textsuperscript{14} The marked dependence of activation energies for arene exchange on ligand modifications described in the previous section should therefore have a pronounced effect on the catalytic performance of these catalyst systems.

![Scheme 3.3. Rate limiting insertion of ethylene into a five-membered titanacycle occurs by partial dissociation of the pendant arene moiety.](image)

The performance of the catalyst systems 1d-g/MAO in ethylene trimerisation was evaluated. Recent studies aimed at reducing the amount of polymer formed in the reaction indicated that the degree of alkylation at the titanium centre has a substantial influence on the productivity and selectivity. Specifically, the performance of precatalysts of the general formula [Cp-arene]TiMe\textsubscript{n}Cl\textsubscript{3-n} was shown to increase on going from n = 0 to n = 3.\textsuperscript{22} Thus, in the catalytic trimerisation experiments with titanium trichloride complexes activated with MAO described here, we employed the ‘premix’ procedure that was found to give improved results for related systems.\textsuperscript{22} Using this procedure, the titanium trichloride precatalyst is (partially) alkylated by reaction with MAO (250 equiv) before it is injected into the autoclave. The results for the ethylene trimerisation studies are shown in Table 3.2. A comparison of runs 1-5 reveals that all precatalysts with a C\textsubscript{1} bridge (1d-f) produce 1-hexene with good selectivity (> 92.5% C\textsubscript{6}, which consists of > 99.5% 1-hexene) upon activation with MAO. The C\textsubscript{2}-bridged compounds make very little (1g) or no (1h) 1-hexene under the same conditions, while also no significant amounts of polymer are obtained. Due to the strong Ti-arene interaction in the latter two systems (vide supra), the Cp-arene ligand loses its hemilabile character and consequently the catalytic activity is quenched. Since the rate-determining step in the catalysis involves (partial) dissociation of the pendant arene, weak arene binding should provide the most active catalyst. Although the initial kinetics appear to be the fastest for 1d/MAO, the optimum productivity over the full 15 min runtime is achieved with 1f/MAO, suggesting that the stability imparted by a stronger Ti-arene
interaction is important to stabilise the active species and prevent catalyst decomposition. The trimerisation activity of the titanium trimethyl complexes $3d$-$3h$ (generated in situ from $2d$-$h$) is somewhat higher than that for the corresponding trichlorides/MAO, except for $3e$, which makes predominantly polyethylene. This increase in activity is in line with previous studies that showed that a higher degree of alkylation results in better catalytic performance. The reason for the difference in catalytic ethylene conversion for $1e$/MAO compared to $3e$ is as yet unclear. However, the ethylene uptake profile for run 7 shows a rapid decay of activity in the first minute, which is followed by an increase in ethylene consumption after ca. 2 min, which may suggest that a decomposition product of $3e$ is responsible for the polymer formation.

### Table 3.2. Catalytic ethylene conversion with the $1d$-$h$/MAO and $3d$-$h$ catalyst systems.

<table>
<thead>
<tr>
<th>run</th>
<th>catalyst$^a$</th>
<th>$C_6$ (g)</th>
<th>PE (g)</th>
<th>$C_6$ selectivity (wt%)</th>
<th>$C_6$ productivity$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1d$/MAO</td>
<td>12.5</td>
<td>0.21</td>
<td>98.3</td>
<td>997</td>
</tr>
<tr>
<td>2</td>
<td>$1e$/MAO</td>
<td>2.5</td>
<td>0.20</td>
<td>92.5</td>
<td>197</td>
</tr>
<tr>
<td>3</td>
<td>$1f$/MAO</td>
<td>20.0</td>
<td>0.10</td>
<td>99.5</td>
<td>1602</td>
</tr>
<tr>
<td>4</td>
<td>$1g$/MAO</td>
<td>0.3</td>
<td>0.05</td>
<td>85.9</td>
<td>23</td>
</tr>
<tr>
<td>5</td>
<td>$1h$/MAO</td>
<td>none</td>
<td>0.17</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>$3d$</td>
<td>7.8</td>
<td>0.27</td>
<td>96.7</td>
<td>1045</td>
</tr>
<tr>
<td>7</td>
<td>$3e$</td>
<td>0.4</td>
<td>4.19</td>
<td>9.6</td>
<td>59</td>
</tr>
<tr>
<td>8</td>
<td>$3f$</td>
<td>20.6</td>
<td>0.18</td>
<td>99.1</td>
<td>2747</td>
</tr>
<tr>
<td>9</td>
<td>$3g$</td>
<td>0.3</td>
<td>0.21</td>
<td>56.9</td>
<td>37</td>
</tr>
<tr>
<td>10</td>
<td>$3h$</td>
<td>none</td>
<td>0.27</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ $1d$-$h$: 5 µmol catalyst precursor, premixed with 250 equiv MAO, total 500 equiv MAO, 10 bar, 30 °C, 15 min. $3d$-$h$: 3 µmol catalyst precursor ($2d$-$h$), 1.05 equiv ammonium borate [R$_2$NMMeH][B(C$_6$F$_5$)$_4$], 40 mg MAO scavenger, 10 bar, 30 °C, 15 min.$^b$ $>99.5$% 1-hexene. $^c$ in g(C$_6$)·mmol(Ti)$^{-1}$·bar$^{-1}$·h$^{-1}$.

Several related ligand modifications were studied in our group previously, and the results presented here are in agreement with general trends gleaned from these experiments. Although ligand substituent effects are non-additive and there appears to be a delicate balance in activity and stability leading to optimal catalyst productivity, it is clear that the hemilabile behaviour of the pendant arene moiety is crucial to obtain a good catalyst. It should be noted here that also other pendant donor groups have been used to obtain titanium systems capable of producing 1-hexene. For complexes with cyclopentadienyl...
ligands bearing a thienyl substituent the trimerisation activity was shown to be highly
dependent on the position of the (potentially) coordinating S atom (2-thienyl vs. 3-thienyl),
indicating that in this case $\eta^1$-S coordination predominates over $\eta^5$-coordination of the
thienyl ring. Also, half-sandwich titanium complexes with pendant ethereal groups have
been reported, but in both cases the ethylene trimerisation activities are orders of
magnitude lower than for the Cp-arene titanium systems.

3.3. COMPUTATIONAL STUDIES ON \textit{ansa}-CP-ARENE TITANIUM(IV)
COMPLEXES

3.3.1. Optimised geometries and molecular orbital analysis

The \textit{ansa}- Cp-arene titanium dimethyl cations were studied by DFT calculations (the
anions were omitted, see Experimental Section for details). A series of computational
papers has appeared that focused on the energetic landscape of titanium-catalysed ethylene
trimerisation, the influence of changing the metal centre to Zr/Hf, as well as
different substituents on the pendant arene moiety (for M = Zr). With the experimental
trends in metal-arene interaction strength in hand, we feel that a detailed analysis of the
factors governing the metal–arene interaction by computational methods is appropriate. The
optimised structures of the cationic titanium complexes (3a’-3c’) adopt the \textit{ansa}- Cp-arene
coordination geometry, in overall agreement with the X-ray crystal structures of 3a-c
described in Chapter 2. The main difference lies in the Ti-C(arene) bond distances, which
are on average larger by 0.16 and 0.14 Å for 3b’ and 3c’, respectively. The energy
associated with this elongation is small: the calculated energy of 3b’ using Ti-C(arene)
bond lengths found in the X-ray structure is only 1.3 kcal·mol$^{-1}$ higher in energy compared
to the fully optimised structure. This highlights the relative insensitivity of the metal-arene
interaction (‘softness’) to small geometrical changes. Nevertheless, more pronounced
differences are expected for the ligand modifications described above (e.g., C1 vs. C2
bridge) and attempts to obtain a better understanding from a theoretical viewpoint are
discussed below.

Analysis of the frontier molecular orbitals shows the isolobal relationship between the
‘naked’ \textit{ansa}- Cp-arene titanium(IV) fragment [$\eta^6$-Ar-Z-$\eta^5$-C$_2$H$_4$]$\text{Ti}^{3+}$ (Ar = 3,5-Me$_2$Ph; Z =
CMe$_2$ ((Ti(b)$^{3+}$)); Z = CH$_2$CMe$_2$ (Ti(c)$^{3+}$)) and the well-known bent metallocenes (Figure
3.2). The molecular orbitals for Ti(b)$^{3+}$ and Ti(c)$^{3+}$ have very similar shapes and
relative energies (only those for Ti(b)$^{3+}$ are shown here). The LUMO of Ti(b)$^{3+}$ is the
equivalent of the 1a$_1$ orbital in C$_2$, symmetric bent metallocenes. For comparison, we have
calculated the structure of the analogous ‘naked’ titanium(IV) \textit{ansa}-metallocene complex
H$_2$C(\textit{\eta}^5-C$_2$H$_4$)$_2$Ti$^{2+}$ at the same level of theory (Figure 3.2). The energy of the frontier
molecular orbitals in H$_2$C(\textit{\eta}^5-C$_2$H$_4$)$_2$Ti$^{2+}$ is higher by $\sim$4 eV compared to Ti(b)$^{3+}$, due to the
difference in charge (Ti(b)$^{3+}$ is considerably more electrophilic). The interaction between a
bent metallocene fragment and two additional anionic $\sigma$-donor ligands, e.g. Cl$^-$ or Me$^-$, has
been explained based on MO considerations in the seminal work of Lauher and Hoffmann, and a similar analysis applies for the complexes described here. Thus, the bonding of two Me groups such as in the titanium(IV) dimethyl cations studied in this work (3a-h) occurs mainly by interaction with the orbital that is the equivalent of the \( b_2 \) orbital in bent metallocenes, resulting in a MO scheme as shown in Figure 3.3.

Figure 3.2. Frontier molecular orbitals of \([\eta^6-Ar-CMe_2-\eta^5-C_5H_4]Ti^{3+}\) (Ti(b))\(^{3+}\), top), \(H_2C(\eta^5-C_5H_4)_2Ti^{2+}\) (bottom), and their corresponding energies (eV).
Figure 3.3. Molecular orbital interaction scheme for bonding of two \( \sigma \)-donor ligands (Me\(^+\)) to \([ansa\text{-}Cp\text{-arene}]\text{Ti}^{3+}\) (symmetry labels as for \( C_2v \) symmetric bent metallocenes).

3.3.2. Charge decomposition analysis

Donor-acceptor complexes of transition metals may be described by the Dewar-Chatt-Duncanson model for coordination of \( \pi \)-conjugated ligands to a transition metal centre.\(^{29,30}\) In principle there are two contributions to such an interaction: (i) donation from a filled ligand orbital into an empty orbital on the metal, and (ii) backdonation from an occupied metal d-orbital into an empty \( \pi^* \)-orbital of the ligand (Figure 3.4). The titanium dimethyl cations discussed here and in Chapter 2 consist of a titanium(IV) metal centre (lacking d-electrons), and the most prominent interaction of the CpTiMe\(_2^+\) fragment with the arene moiety is expected to involve donation from the arene \( \pi \)-system into an empty metal d-orbital.

Analysis of the donor-acceptor interaction was performed using the charge decomposition analysis (CDA) method developed by Frenking and co-workers (see Experimental Section for details).\(^{31,32}\) This partitioning scheme has been found useful in the analysis of donation and backdonation interactions in transition metal complexes.\(^{32}\) In this context it is important to realise that the absolute values obtained from the CDA scheme are not very meaningful (for instance, the values are quite sensitive to the choice of basis.
Nevertheless, the analysis of a series of related compounds that are calculated using the same method should allow qualitative or semi-quantitative trends to be extracted.

Here, we use the CDA method to evaluate the relative amount of donation from the arene ligands to the metal centre in representative *ansa*-Cp-arene titanium dimethyl cations (for the sake of completeness, also the ‘naked’ complexes Ti(b)\textsuperscript{3+}/Ti(c)\textsuperscript{3+} were included). We chose to focus on ligand modifications that were experimentally shown to induce the largest difference in arene binding strength. More specifically, we have studied complexes that have the same bridge (CMe\textsubscript{2}) but differ in the arene part (Ar = Ph, \textit{3a}′ vs. 3,5-Me\textsubscript{2}Ph, \textit{3b}′), as well as complexes that have the same arene moiety (3,5-Me\textsubscript{2}Ph) but different bridge lengths (Z = CMe\textsubscript{2}, \textit{3b}′ vs. CH\textsubscript{2}CMe\textsubscript{2}, \textit{3c}′). For the charge decomposition routine, the complex has to be described by two separate parts (donor/acceptor). Here we take the arene moiety as the donor fragment, while the acceptor fragment consists of the titanium atom with cyclopentadienyl and methyl ligands. The DFT optimised geometry of the respective *ansa*-Cp-arene titanium species was taken and the cyclopentadienyl-arene ligand was split by removing the bridging atom(s), as depicted schematically in Scheme 3.4. A hydrogen atom was added to the cyclopentadienyl and arene moieties at the position of the bridge in order to obtain closed-shell fragments. The complexes thus obtained (\textit{IIIa-c}) were used without further optimisation to model the geometries of various *ansa*-Cp-arene coordinated titanium cations. In addition, the structure of [Cp]\textsuperscript{[\eta\textsuperscript{6}-1,3,5-Me\textsubscript{3}C\textsubscript{6}H\textsubscript{3}]}TiMe\textsubscript{2}\textsuperscript{+} was optimised for comparison, which converges to a minimum on the potential energy surface that has a geometry that is similar to the C\textsubscript{2}-bridged complex 3c or structurally characterised analogues without bridging atom (e.g., Cp(centroid)-Ti-Ar(centroid) angle: \textit{III}′: 134.4°; \textit{3c}: 130.9°; Cp'(\eta\textsuperscript{6}-toluene)HfMe\textsubscript{2}\textsuperscript{+}: 134°)\textsuperscript{16,35} The charge decomposition procedure we employed gives a measure of (fragment) molecular orbital interactions between the two closed-shell fragments as a result of complex formation, for which four terms (\textit{d}, \textit{b}, \textit{r} and \textit{\Delta}) are obtained. The donation term \textit{d} is due to mixing of occupied orbitals on the arene fragment with unoccupied orbitals on the CpTiMe\textsubscript{2}\textsuperscript{+} fragment; the backdonation \textit{b} is the result of mixing of empty arene orbitals with filled metal orbitals. The
remaining terms $r$ (repulsive polarisation) and $\Delta$ (non-classical rest term) are caused by interaction between filled and empty orbitals of both fragments, respectively. This last term should be vanishingly small in case of a true donor-acceptor complex: if not, the compound is more appropriately described by the interaction of two open-shell fragments (i.e., with a covalent bond). Results of the charge decomposition analysis for these compounds are collected in Table 3.3.

![Scheme 3.4. Construction of arene and CpTiMe$_2^+$ fragments for the charge decomposition analysis.](image)

**Table 3.3. Charge decomposition analysis of the metal-arene interaction.**

<table>
<thead>
<tr>
<th>L = arene</th>
<th>$d$ (e)</th>
<th>$b$ (e)</th>
<th>$r$ (e)</th>
<th>$\Delta$ (e)</th>
<th>$d/b$</th>
<th>$E_b^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(b)$^{3+}$</td>
<td>0.666</td>
<td>0.062</td>
<td>-0.543</td>
<td>-0.005</td>
<td>10.7</td>
<td>161.3</td>
</tr>
<tr>
<td>Ti(c)$^{3+}$</td>
<td>0.669</td>
<td>0.040</td>
<td>-0.208</td>
<td>-0.037</td>
<td>16.7</td>
<td>192.3</td>
</tr>
<tr>
<td>IIIa</td>
<td>0.345</td>
<td>0.068</td>
<td>-0.721</td>
<td>-0.044</td>
<td>5.1</td>
<td>-16.2</td>
</tr>
<tr>
<td>IIIa$^b$</td>
<td>0.549</td>
<td>0.048</td>
<td>-0.696</td>
<td>-0.020</td>
<td>11.4</td>
<td>-10.7</td>
</tr>
<tr>
<td>IIIb</td>
<td>0.569</td>
<td>0.051</td>
<td>-0.702</td>
<td>-0.020</td>
<td>11.2</td>
<td>4.3</td>
</tr>
<tr>
<td>IIIc</td>
<td>0.644</td>
<td>0.063</td>
<td>-0.288</td>
<td>-0.038</td>
<td>10.2</td>
<td>39.2</td>
</tr>
<tr>
<td>III$^*$</td>
<td>0.663</td>
<td>0.059</td>
<td>-0.255</td>
<td>-0.046</td>
<td>11.2</td>
<td>46.6</td>
</tr>
</tbody>
</table>

$^a$ the total bonding energy is the difference between the sum of the two fragments and the complex (kcal·mol$^{-1}$). $^b$ calculated using the geometry of IIIb, but without methyl substituents on the arene.

As anticipated, from the CDA results it is clear that for the $d^0$ titanium(IV) cations described here, the largest contribution to the bonding is due to interaction between the occupied arene orbitals with empty metal-based orbitals ($d$), and the amount of backdonation $b$ is negligible ($d/b > 10$). The situation is quite different for titanium(II)
species, and a detailed analysis of these will be presented in Chapter 4. The total arene→Ti donation \( d \) is highest for species that represent the C\(_2\) bridged Cp-arene compounds (Ti(c))\(^{3+} > \) Ti(b)\(^{3+}; \) IIIc > IIIb). The largest individual orbital contributions to the donation term \( d \) for the dimethyl titanium(IV) complexes IIIb/c are located in the HOMO-4 and HOMO-5 (Figure 3.5). Inspection of these orbitals reveals that the metal-arene interaction is mainly the result of overlap of the filled \( \pi \)-system of the aromatic ring with empty d-orbitals on the titanium centre. Moreover, a comparison of these orbitals in IIIb and IIIc reveals that the strained ansa-Cp-arene coordination for the C\(_1\)-model compound IIIb leads to a most pronounced decrease in arene→Ti donation due to the HOMO-5. This particular orbital has prominent contributions from the arene \( \pi \)-system that is delocalised over the meta- and para-positions of the C\(_6\) ring. The strained ansa-Cp-arene coordination in complexes with a C\(_1\) bridge prevents a close approach of this part of the arene ring to the metal centre.

![Figure 3.5](image)

**Figure 3.5.** Representation of orbitals that are mainly involved in the donation term \( d \) in ansa-Cp-arene titanium(IV) cations, and their contribution to \( d \) (between brackets).

The difference in energy between the separated fragments and the complex allows an evaluation of the total bonding energy of the interaction. Analysis of these bonding energies (\( E_b \), Table 3.3) shows that there is a large increase in metal–arene binding strength on going from a complex with C\(_1\) bridge (IIIb), via C\(_2\) (IIIc), to a compound without ansa-bridge (III”). The negative value for IIIb is puzzling at first sight, but this is likely related to the fact that the hydrogen atoms that are added after fragmentation of the ligand give rise to some steric repulsion. In any case, the 43.5 kcal·mol\(^{-1}\) difference in binding energy by changing the nature of the bridge is primarily associated with the degree of orbital overlap between the CpTiMe\(_2\)\(^+\) and arene fragments. There is only a minimal effect of the energy and geometry of the individual fragments in IIIb vs. IIIc: the geometries of the fragments are superimposable and the energies virtually identical (within 3 kcal·mol\(^{-1}\)).

The optimised geometry of 3a’, for which Ar = Ph instead of 3,5-Me\(_2\)Ph, has Ti-C(arene) distances that range from 2.541 (C\(_{ipso}\)) to 3.327 Å (C\(_{para}\)), which is relatively long
compared to those in 3b’ (2.498-3.119 Å). As a consequence, the charge decomposition analysis on IIIa (derived from 3a’) shows the arene to be a worse donor (\(d = 0.345\) e vs. 0.569 e in IIIb). To exclude the effect of changes in the ansa-Cp-arene bonding geometry, we additionally performed the charge decomposition analysis for IIIa with all Ti-C(arene) distances kept the same as in IIIb. As expected, the resulting donor-ability is lowered (\(d = 0.549\) e) compared to IIIb due to the decrease in electron-density in the arene ring, and the metal-arene interaction becomes weaker (\(\Delta E_b = 6.4\) kcal·mol\(^{-1}\)).

3.4. CONCLUSIONS

The quantitative information on the barrier for site exchange in desymmetrised ansa-Cp-arene titanium(IV) cations obtained by variable-temperature and 2D NMR spectroscopy corroborates that the metal-arene interaction strength increases considerably when changing from C\(_1\)- to C\(_2\)-bridged compounds, such that the hemilabile character is effectively quenched. The computational results given here provide a rationale in terms of orbital overlap for the pronounced dependence of the arene binding strength on the bridge length between the cyclopentadienyl and arene fragments. Smaller effects were observed for variations in arene and bridge substituents. The catalytic ethylene trimerisation studies reveal a trend that is consistent with the view that ethylene insertion into metalacyclic intermediates is rate-limiting and involves (partial) dissociation of the coordinated arene. Nevertheless, differences in overall catalytic performance that result from small changes in ligand structure are additionally complicated by stability issues. The rational design of improved Cp-arene titanium catalysts for ethylene trimerisation is therefore not straightforward, as it should also involve features that improve catalyst stability, and the nature of the catalyst decomposition process is unknown as yet. Nevertheless, it is clear that strained ansa-Cp-arene coordination due to a small bridging group is essential.
3.5. EXPERIMENTAL SECTION

**General Considerations.** For experimental details, see the Experimental Section in Chapter 2. In addition: Ethylene (AGA polymer grade) was passed over BASF R3-11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4 Å). \([\text{R}_2\text{NMeH}]\text{[B(C}_6\text{F}_5)_4]\) \((R = \text{C}_{16}\text{H}_{31}–\text{C}_{18}\text{H}_{35}, 6.2 \text{ wt% B(C}_6\text{F}_5)_4\) in Isopar, Dow Chemicals), and MAO (4.9 wt% Al in toluene, Akzo Nobel) were used as received. Variable temperature NMR spectra were recorded on a Varian Inova 500 spectrometer. Coalescence temperatures were determined on equilibrated samples (allowing ca. 10 min for the temperature to stabilise). Sample temperatures were determined using a Pt-100 resistance that was inserted at the sample position in the probe. EXSY spectra were acquired using a modified NOESY pulse sequence (incorporating an additional z-gradient during mixing time \(\tau_{\text{mix}}\)). In the indirectly detected dimension 256 complex points were collected with 2 scans and 2048 points per increment. Zero-filling was applied to obtain \(2048 \times 2048\) data points, and Gaussian line-broadening was applied in both dimensions prior to Fourier transformation. Integration of the EXSY spectra recorded at 18.4 °C with mixing times of 0.4, 0.7, 0.8 and 0.9 s was performed using the Gaussian fit routine implemented in Sparky. Cross-peak volumes of the spectra were normalised \((I_{x}/I_{d})\) and the data points were fitted against equation \((1)^{38}\) by non-linear regression.

\[
\frac{I_x}{I_d} = \frac{1 - e^{-2k\tau_{\text{mix}}}}{1 + e^{-2k\tau_{\text{mix}}}} \quad \text{with} \quad k = \frac{k_b T}{h} e^{\frac{\Delta G^2}{RT}}
\]

**General procedure for trimerisation experiments.** In the glovebox, (pre-)catalyst stock solutions were made \((1\text{d}-1\text{h}: 50 \mu\text{mol}; 2\text{d}-2\text{h}: 30 \mu\text{mol})\) in 10 mL of toluene and stored at -30 °C. From these solutions, 1.0 mL portions were used for trimerisation experiments. All trimerisation runs were performed in a 1.0 L stainless steel autoclave, pre-dried under reduced pressure, charged with 200 mL of dry toluene, equilibrated at 30 °C, and pressurised with 10 bar of ethene. For the runs with trichlorides \(1\text{d}-1\text{h}\), 250 equiv of MAO were injected first into the autoclave (using a pneumatically operated injector). In the glovebox, the catalyst solution was mixed with 250 equiv of MAO and rapidly (within 1 min after mixing) injected into the autoclave (total Al/Ti ratio = 500). For the runs with \(2\text{d}-2\text{h}\), 1.05 equiv of \([\text{R}_2\text{NMeH}]\text{[B(C}_6\text{F}_5)_3]\) \((R = \text{C}_{16}\text{H}_{31}–\text{C}_{18}\text{H}_{35}, 6.2 \text{ wt% B(C}_6\text{F}_5)_3\) in Isopar, DOW Chemicals) mixed with ca. 40 mg of MAO as scavenger, were injected first. The reaction was started by injecting the solution of the titanium trialkyl \((2\text{d}-2\text{h})\). The ethene pressure was kept constant during the reaction by replenishing flow. The reactor was stirred for 15 min, a known amount of cyclohexane was injected, after which a sample of the liquids was taken for GC analysis. The reactor was vented, the polymeric material collected, washed with acidified ethanol and dried in a vacuum oven at 80 °C. Integration of the cyclohexane and 1-hexene peaks in the GC from the liquid samples gives the amount of 1-hexene that is produced.
Computational Studies. Calculations were performed with the Gaussian03 program using density functional theory (DFT).\textsuperscript{39} Geometries of the cations 3a-c were fully optimised starting from the X-ray structures using the B3LYP exchange-correlation functional with the LANL2DZ basis set on the metal centre, and 6-311G(d) basis sets on all other atoms. The anions were omitted in the calculations. Optimisations were performed without (symmetry) constraints, and the resulting structures were confirmed to be minima on the potential energy surface by frequency calculations (number of imaginary frequencies = 0). Charge decomposition analysis was performed using the CDA program by Dapprich and Frenking.\textsuperscript{40} The input for the CDA program was generated from single point calculations on the appropriate species (without bridging atoms, as described in the main text) with double-$\zeta$ basis sets used throughout (LANL2DZ on the metal, 6-31G(d) on all non-metal atoms). Geometry optimisation of 3b using double-$\zeta$ basis sets on all atoms resulted in a structure with metrical parameters that are virtually identical to the ones obtained using 6-311G(d) on the non-metal atoms. For visualisation of the computed structures and molecular orbitals the program MOLEKEL 4.3 was used.\textsuperscript{41}

3.6. REFERENCES

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Hemilabile ansa-Cp-arene coordination and its relevance to catalysis

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