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Conformational studies of ligand-template assemblies and the consequences for encapsulation of rhodium complexes and hydroformylation catalysis†

Ivo Jacobs,a Adri C. T. van Duin,b Arjan W. Kleij,‡a Mark Kuil,a Duncan M. Tooke,c Anthony L. Spekac and Joost N. H. Reek*ac

The second coordination sphere around a transition metal catalyst can contribute to the activity and selectivity that it displays. In this paper we present encapsulated catalysts using a template-ligand assembly strategy based on Zn(salphen) building blocks, and show that these have significantly different properties in catalysis than previously reported Zn(porphyrin)-based analogues. The conformational properties of tris-Zn(salphen) capsule catalysts were examined by a combination of solid state and solution phase analytical methods, as well as computational techniques. We found that as a result of the ability of the salphen-based capsules to adopt different conformations compared to porphyrin-based capsules, less stringent constraints are enforced to the catalytic centre, resulting in different catalyst selectivities displayed by the rhodium complexes enclosed.

Introduction

Self-assembled molecular capsules with hollow structures can encapsulate smaller guest molecules within their cavities.1 Since the 1990s, various research groups have investigated the application of such capsules as nanoreactors.2 A diversity of chemical processes, both stoichiometric and catalytic, has been carried out within molecular capsules.3 Reactions can be accelerated, as shown for example by Raymond and coworkers. They demonstrated that acid-catalyzed reactions can be carried out inside nano-environments even if the outside conditions are basic.4 Also the selectivity of a chemical process can be changed completely, as shown by Fujita et al. in the Diels–Alder reaction5 and this particular example, where unique selectivities are obtained, shows the influential nature of the finite micro-environment within the capsule. Such unusual selectivities are generally not achieved using traditional catalytic approaches. Although the field of supramolecular capsular catalysis is still in its developmental stage, several successful examples of reactions carried out within self-assembled nanoreactors have appeared and demonstrate the power of the concept. Detailed studies are required to fully understand the mechanisms behind the effects observed when carrying out reactions in these confined spaces.

We have previously reported a general strategy to encapsulate phosphine ligands and metal complexes thereof (Scheme 1).6 The strategy is based on template-ligands, which are building blocks that have one type of coordination site for the transition metal that is active in catalysis, and another type of coordination site used in the self-assembly of the capsule. Initially we used Zn(π)porphyrin building blocks for the assembly process. A tenfold increase in conversion and reversed regio-selectivity (i.e., linear-branched ratio) was found when using 3a in the rhodium catalysed hydroformylation of 1-octene. When using internal octenes, a fourfold increase in yield was found as well as unprecedented selectivity.7 In order to extend the diversity of the building blocks and to vary the size and/or shape of the catalytic capsules, we also used Zn(π)salphens.8 These are easier to prepare than Zn(π)porphyrins, and can be structurally modified using modular approaches.9 Initial results have also shown that with these building blocks we obtained more active catalysts with selectivities generally in between those of the non-encapsulated Rh–phosphine complex and the porphyrin-based capsule. The interaction between the Zn(salphen) building blocks and the
pyridyl fragments of the phosphine template is stronger, which apparently did not translate to higher selectivities.

In this paper we provide insight into the origin of this difference supported by detailed investigations of the structure of the salphen-based capsules both in the solid state and in solution. Computational studies and solution-phase NMR have been used to show the conformational behaviour of these ligands in solution. This conformational flexibility of the encapsulated ligands affects the coordination environment around the transition metal centers, and ultimately the catalytic performance.

Results and discussion

Effects of the encapsulation by porphyrin or salphen units on hydroformylation catalysis

Before discussing the conformational behavior we will summarize the differences in catalytic behaviour observed for the capsules based on porphyrins and various zinc(II)salphens. In Tables 1–3 some of the previously reported results in the hydroformylation of various substrates (Scheme 2) using encapsulated catalysts based on several zinc-containing building blocks and the meta-trispyridylphosphine template are summarised. In addition, we carried out reactions with shorter reaction times such that the conversion indicates the relative reaction rate (Table 4).

Table 1 Results of the rhodium catalysed hydroformylation of 1-octene with trispyridylphosphine and the building blocks illustrated in Scheme 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Yield</th>
<th>TOF</th>
<th>C1/C2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1d</td>
<td>1</td>
<td>31 (6)</td>
<td>5 (3)</td>
<td>2.3 (2.9)</td>
</tr>
<tr>
<td>2e</td>
<td>1 + 2a</td>
<td>52</td>
<td>23</td>
<td>0.56</td>
</tr>
<tr>
<td>3</td>
<td>1 + 2b</td>
<td>97</td>
<td>16</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td>1 + 2c</td>
<td>97</td>
<td>16</td>
<td>1.0</td>
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<tr>
<td>5</td>
<td>1 + 2d</td>
<td>97</td>
<td>16</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 2 Results of the rhodium catalysed hydroformylation of 2-octene with trispyridylphosphine and the building blocks illustrated in Scheme 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Yield</th>
<th>TOF</th>
<th>C2/C3</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>17</td>
<td>2</td>
<td>1.3</td>
</tr>
<tr>
<td>2</td>
<td>1 + 2a</td>
<td>32</td>
<td>5</td>
<td>0.11</td>
</tr>
<tr>
<td>3</td>
<td>1 + 2b</td>
<td>47</td>
<td>7</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>1 + 2c</td>
<td>48</td>
<td>7</td>
<td>0.86</td>
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</table>

Table 3 Results of the rhodium catalysed hydroformylation of 3-octene with trispyridylphosphine and the building blocks illustrated in Scheme 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Yield</th>
<th>TOF</th>
<th>C3/C4</th>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>26</td>
<td>4</td>
<td>0.98</td>
</tr>
<tr>
<td>2</td>
<td>1 + 2a</td>
<td>45</td>
<td>6</td>
<td>0.31</td>
</tr>
<tr>
<td>3</td>
<td>1 + 2b</td>
<td>60</td>
<td>9</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>1 + 2c</td>
<td>63</td>
<td>9</td>
<td>0.98</td>
</tr>
</tbody>
</table>

The difference between the non-encapsulated catalyst and the porphyrin-based capsule (entries 1 and 2 in Tables 1–3 respectively) is clear: the average TOF increases from 3 to 23 for 1-octene, and the C1/C2 product ratio changes from 2.9 to 0.56. Also for the internal octenes the activity increases (2–5), and a profound effect on the selectivity is observed. For 2-octene the C2/C3 ratio changes from 1.3 to 0.11, and for 3-octene the C3/C4 ratio changes from 0.98 to 0.31. This shows that the catalyst can distinguish between the carbon centers at the 3- and 4-position of the substrate (i.e., between an ethyl and an n-butyl group). This effect represents one of the unique examples of an unequalled selectivity induced by a nano-environment.

When Zn(II)salphens are used for encapsulating the hydroformylation catalyst, the activity is in some cases still higher compared to the non-encapsulated ligands, as is apparent from the average TOFs reported in entries 1 and 3–6. From Table 4 it...
can be seen that at short reaction times the average TOFs vary quite significantly when different salphen building blocks are applied. The TOFs range from 12 to 38, which means that the slowest encapsulated catalyst 2f is slower than the non-encapsulated catalyst. However, none of the catalysts based on salphen building blocks converts 1-octene with a higher TOF than the porphyrin-based capsule. For the internal octenes, the salphen-based capsules are also slightly faster than the porphyrin-based ones with TOFs up to 7 for 2-octene and up to 9 for 3-octene. The selectivities are in between those of the non-encapsulated catalyst and the porphyrin-based capsule. For the internal octenes, the salphen-based capsules exhibit two conformations. Left the “in” conformation, right the “out” conformation. In the “out” conformation the Zn ion is located 0.069(4) Å above the basal plane (84%) defined by the N- and O donor atoms of the salphen ligand.13

It is sterically impossible for the porphyrin-based capsule to be in the “out” conformation according to molecular modelling. A recent X-ray molecular structure of the capsule based on tris-meta-pyridylphosphine and 3a shows that it is only in the “in” conformation in the solid state.14 If these salphen based complexes are also able to adapt these out conformations in solution, this would provide a clear explanation for the different selectivities that these complexes induce. The difference in the solid-state structure can, however, be caused by packing effects, and does not necessarily represent the structures present in solution. Therefore, we next studied these supramolecular ligands in solution, to examine if this conformational flexibility actually plays a significant role.

Ruthenium Salphen Complexes as Analogs for Zn(II)Salphen

From NMR titrations that were performed previously to establish the formation of assemblies of type 3 (Scheme 1), it is clear that the building blocks are in fast exchange on the NMR timescale despite a strong pyridyl-zinc interaction ($K_{ass} \sim 10^5$ M$^{-1}$).8,9 NMR analysis of the Zn(II)salphen-based complexes therefore does not give any information about the conformational dynamics. Low-temperature NMR experiments of the Zn(salphen) based assemblies 3 (down to $-90$ °C) only give rise to a single set of $^1$H NMR and $^{31}$P NMR signals. As at these temperatures the pyridyl–zinc complex is still in fast exchange on the NMR timescale, the single set of signals does not mean that co-existence of the two conformations (in and out) can be ruled out. Therefore, we have studied the conformational dynamics of these self-assembled capsules using Ru(II)salphen

### Table 4

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Yield$^b$</th>
<th>TOF$^c$</th>
<th>C1/C2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>27</td>
<td>16</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
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<tr>
<td>3</td>
<td>1 + 2c</td>
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<td>4</td>
<td>1 + 2e</td>
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<td>13</td>
<td>1.9</td>
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<td>5</td>
<td>1 + 2f</td>
<td>21</td>
<td>12</td>
<td>1.8</td>
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<tr>
<td>6$^d$</td>
<td>1 + 2a</td>
<td>44</td>
<td>126</td>
<td>0.60</td>
</tr>
</tbody>
</table>

$^a$ All experiments were performed at 25 °C in toluene, with a substrate/catalyst ratio of 1000. The reaction time was 16 h. See Table S1 (ESI) for more details. $^b$ In percent. $^c$ Average TOF in (mol aldehyde) (mol Rh)$^{-1}$ h$^{-1}$, based on conversion. $^d$ Substrate/catalyst ratio was 5000, reaction time was 18 h.
building blocks. Ru(II)salphen complexes are also known to form strong bonds with pyridines, and the exchange rates between coordinated and free pyridyl are slow on the NMR timescale. As the same salphen framework can be used, the size of the building block is very similar to Zn(II)salphens. The Ru(II)salphens have a CO coordinated opposite to the axial position of the pyridine donor, but since this will be on the outside of the capsule this will not interfere with the formation of capsule structure.

DFT calculations were performed to show the similarities and differences between the Zn(II)salphen–pyridyl and the Ru(II)salphen–pyridyl complexes. These calculations were performed using the B3LYP functional and the DGDZVP basis set. An energy profile was calculated for the rotation over the Npyr–metal bond (Fig. 2). In Fig. 3 the energy is shown as a function of the Osal–M–Npyr–Co,pyr torsion angle, and in Fig. 4 the length of the Npyr–metal bond is shown. The Zn-complex has its energy minimum when the pyridine plane is more or less parallel to the direction of the Zn–O bonds, and the bond length is intermediate at 2.16 Å. The energy barrier associated with this rotation is very small amounting to 0.5 kcal mol$^{-1}$. The Ru(II)-complex, however, has its global minimum when the pyridine plane is perpendicular to the O–O line, and a local minimum when it is parallel to this line. The bond length at the global minimum is 2.24 Å with a still relatively low rotational barrier of 3 kcal mol$^{-1}$. From these calculations it can be concluded that both complexes have virtually free rotation around the M–Npyr bond. As the difference in the M–pyridyl distance is less than 0.1 Å the size and the shape of the capsule that is formed is virtually the same.

NMR analysis of Ru(II)salphen based complexes

NMR titrations were performed in $d_8$-toluene with a fixed concentration of template-ligand 1 containing three pyridyl units (0.1 mM) and by gradually increasing the amount of 2g or 2h (0 to 0.3 mM). The $^1$H and $^{31}$P{1H} spectra clearly demonstrate the slow exchange between the free and associated components. Separate peaks for the free phosphine, the 1 : 1 complex, the 2 : 1 complex and the 3 : 1 complex were observed, an observation also clearly visible in the $^{31}$P NMR spectra (Fig. 6).

In the $^1$H NMR spectra (Fig. 7) the aliphatic region shows distinct peaks for all these associated states because the tert-butyl groups shift upon coordination. Interestingly, the tert-butyl groups of salphen 2h give two signals each in the 2 : 1 complex. This is not due to inequivalency of the salphens but because the $C_{2v}$ symmetry of the salphens is broken in the 2 : 1 complex (see Fig. 5). In the 3 : 1 complex the $C_{3v}$ symmetry is restored, and the tert-butyl groups give rise to only one peak. This means that the trispyridylphosphine template can be considered to have $C_{3v}$ symmetry in all its forms: free, in the 1 : 1 complex, in the 2 : 1 complex, and even in the 3 : 1 complex. From this we can conclude that the symmetry inversion of the trispyridylphosphine unit is fast on the NMR timescale, even in its fully encapsulated form. If the inversion would be slow on the NMR timescale, we would observe the trispyridylphosphine as a $C_{3v}$ symmetric entity, and the whole complex would have lower symmetry. Based on the simplicity of the NMR patterns we can also conclude that the salphens can freely rotate around the Ru–Npyr bond, in line with the energy barriers that we computed.

The signals in the aromatic region (see the ESI†) display the same symmetry for the various complexes: the 1 : 1 complex gives one set of signals for the salphen fragment, and two sets of signals (in a 1 : 2 ratio) for the pyridylphosphine. The 2 : 1 complex gives two sets of signals for the salphen groups and two sets of signals for the pyridylphosphine. And finally the 3 : 1 complex gives one set of signals for both the salphen and pyridylphosphine components.
Importantly, the free building blocks and the 1 : 1, 1 : 2 and 1 : 3 complexes can be distinguished by NMR as the Ru–pyridine exchange is slow on the NMR timescale. We expect substantial spectral differences if different capsular conformations are present, but we observe only one set of signals for the 3 : 1 complex. This indicates that either (1) only one conformation exists in solution, or (2) rapid interchange of different conformations occurs on the NMR timescale via a process that does not involve salphen dissociation. In the next section this non-dissociative conformational exchange using molecular dynamics is discussed.

**Molecular dynamics modeling**

The conversion between the “in” and the “out” conformation was studied by molecular dynamics simulations. As pyridyl decoordination may be required for this process, it is important to use a computational model that allows bond breaking. For this reason, we used the ReaxFF reactive force field method for these simulations. ReaxFF has been successfully applied in previous simulations on transition metal–organic interactions. To enable application to the Ru–pyridine systems here we extended the ReaxFF C/O/N/H description, as developed for protein-based materials with P–C, Zn–N and Ru–N bond- and angle parameters against a DFT-based training set, containing P–phenyl and P–CH₃ bonds, Ru–pyridine and Zn–NH₂ and Zn–NH₃ bond dissociation curves. The ReaxFF H/C/N/O parameters successfully reproduce rotational barriers in aromatic and non-aromatic hydrocarbons and heteroatoms and provide a geometry-dependent charge-calculations, indicating that this method is suitable for studying complex rotational barriers in metallo-organic complexes, as described here.

In our molecular dynamics simulations we investigated three types of conformational changes, as shown in Fig. 8. The first is a so-called “propellor flip” (A) of the pyridylphosphine, which only changes the handedness of the pyridylphosphine propellor, but not the up or down orientation of the pyridyl groups. The second conformational change relates to the rotation of the salphen units around the Nₚₚ–Zn or Nₚₚ–Ru bond (B). These two types of rotation were performed as a benchmark, as these are known to be fast on the NMR timescale, thus providing a reference point.

Finally, and most importantly, we studied the pyridyl group rotation (C), which is necessary to go from the “in” to the “out”...
conformation. All these simulations were performed for both the “in” and the “out” conformation of the supramolecular assemblies based on the Zn complex 3b and the Ru complex 3g.

From Fig. 9 and 10 it can be deduced that for both the Zn and the Ru assembly the energy barrier for the propellor flip is much higher for the “out” conformation (35 and 80 kcal mol$^{-1}$, respectively) than for the “in” conformation (20 and 40 kcal mol$^{-1}$, respectively). The calculated energy barriers are higher than would be expected from the NMR measurements, as dynamic processes with barriers higher than 16–20 kcal mol$^{-1}$ should be slow on the NMR timescale. This can be explained by a relatively short timescale used for the simulations (25 ps). While the complexes have plenty of time to equilibrate in the NMR experiment (nanosecond timescale), for example by rotation of the salphen units, this is not the case in the simulation. This can result in higher energy barriers for the simulations than in the experiments.$^{25}$ The relative barriers that are calculated can still be compared. Also for the salphen rotations (Fig. 11 and 12) relatively high barriers were found (up to 35 kcal mol$^{-1}$ for the rotation of a Ru(II)salphen from the “out” conformation), whereas these rotations have also proven to be fast on the NMR timescale.

The barriers for pyridine rotation (Fig. 13 and 14) are in the order of 20 kcal mol$^{-1}$. Since this is lower than the barrier for the propellor flip, which is fast on the NMR timescale, we can conclude that the non-dissociative conformational exchange is also fast on the NMR timescale. This means that the supramolecular ligands 3b and 3g can exist as a mixture of conformations in solution, while the NMR spectra will give an average signal. Based on the current data we do not know the relative amount of each conformer in solution, and the calculations are not sufficiently accurate to predict the relative stability.

Metal complexes

The nature of the active species under hydroformylation conditions was previously determined directly using high-pressure infrared spectroscopy (HP-IR)$^{20}$ for the catalyst based on the
porphyrin capsule comprising 3a. In HP-IR three distinct bands were observed in the carbonyl-stretching region. This means that a monophosphine–rhodium species is formed, which is in line with the HP NMR data and the distinct catalytic properties. For catalysts based on the salphen capsule, only indirect evidence of mono-phosphine species has been reported so far. In previous studies of the catalyst precursor it has been shown that a 2 : 1 mixture of 3f and Rh(acac)(CO)2 in CDCl3 gives rise to two signals in the 31P NMR: a singlet at −20.9 ppm (free ligand), and a doublet at 43.4 ppm with a coupling constant of 182 Hz, which is characteristic for a monophosphine–Rh complex.

We also recorded the HPIR spectrum under actual hydroformylation conditions, which shows the typical bands observed for a mixture of complexes with two phosphorus donor atoms in the ee and ea coordination mode (Fig. 15). The HP-IR spectrum can be simulated relatively well by making a 1 : 1 : 1 linear combination of the equatorial–axial and equatorial–equatorial bis-phosphine complexes and the equatorial monophosphine complex (Fig. 16). In combination with the molecular modeling studies that show rapid exchange between “in” and “out” conformations, we conclude that it is most likely that these salphen-based catalysts are able to adopt “out” conformations upon coordination that do not exclusively enforce formation of mono-phosphine complexes.

Conclusions

By a combination of X-ray analysis, spectroscopic analysis, DFT and ReaxFF molecular dynamics calculations we have been able

Notes and references


11 Hydroformylation experiments were performed in a stainless-steel autoclave with an insert for GC vials to run up to 15 experiments at the same time. The autoclave was equipped with a pressure indicator, and was kept at constant room temperature in an oil bath. Each GC vial was equipped with a stirring bar. In a typical run each GC vial contained 1 ml of a solution of Rh(acac)(CO)2 (0.1 mM), meta-trispyridylphosphine (9 eq.), Zn(salen)phosphine (27 eq.) and octene (1000 eq.). In the cases where salphens were used as an associated building block, diisopropyl-ethylamine (2.5 eq.) was used to protect the salphens from acid-induced autocatalytic demetallation.


13 Crystal structure determination of 3b: C99H102N9O6PZn3, Fw = 1741.04, orange block, 0.22 × 0.2 × 0.14 mm3, trigonal crystal system, space group P31c1, cell parameters: a = 20.8644(4) Å, c = 52.9489(13) Å, V = 19961.8(7) Å3, Z = 8, 204945 reflections were measured on a Nonius KappaCCD diffractometer with a rotating anode and MoKα radiation (graphite mono-chromator, λ = 0.71073 Å) at a temperature of 150(2) K. A multi-scan absorption correction was applied (μ = 0.784 mm–1, 0.68–0.9 transmission). 8702 unique reflections (Rint = 0.0974), of which 7387 were observed [I > 2σ(I)]. The structure was solved with the program DIRDIF21 and refined using the program SHELXL-9722 against F2 for all reflections up to a resolution of θ = 22.48°. Non-hydrogen atoms were freely refined with anisotropic displacement parameters. H atoms were placed at geometrically idealized positions [d(C–H) = 0.98 for methyl H atoms and 0.95 for other H atoms] and constrained to ride on their parent atoms, with Uiso(H) = 1.5Ueq(C) for methyl H atoms and Uiso(H) = 1.2Ueq(C) for all other H atoms. The structure contained disordered solvent molecules, which were taken into account by back- Fourier transformation with PLATON/SQUEEZE23 (SQUEEZE volume = 4202 Å3, recovered number of electrons = 502). 722 refined parameters, 0 restraints. R (obs. refl.): R1 = 0.0538, wR2 = 0.1105. R (all data): R1 = 0.0746, wR2 = 0.1185. Weighting scheme w = 1[σ2(Fo) + (0.0367P)2 + 1.1877P], where P = (Fo2 + 2Fe2)/3. GoF = 1.179. Residual electron density between –0.394 and 0.387 e Å–3. Checking for additional symmetry was performed with the program PLATON.24 CCDC 831697.


18 NMR measurements were recorded on a Varian 500 NMR spectrometer. The titration experiments were performed as follows: a sample containing 0.75 ml of a solution of 0.1 mM tris-<i>m</i>-pyridylphosphine in <i>d</i><sub>8</sub>-toluene was prepared, and measured. To this sample, 0.1 ml of a solution of Ru(II)salphen (0.375 mM) and tris-<i>meta</i>-pyridylphosphine (0.1 mM) was added for each successive measurement.


20 High-pressure FT-IR was performed in a stainless steel 50 ml autoclave equipped with INTRAN windows (ZnS), a mechanical stirrer and a pressure transducer. The spectra were recorded with a Nicolet 510 FT-IR spectrophotometer. The high-pressure infrared experiments were performed in a high-pressure infrared autoclave that was degassed and filled with argon before use. In a typical experiment 

\[ P(\text{meta-pyr})_3 \text{(95 \mu mol, 25 mg)} \text{ and ZnTPP (284 \mu mol, 192 mg)} \text{ in DCM (13 ml)} \text{ were injected into the autoclave. The autoclave was flushed three times with syngas, and pressurized to 20 bar. The background spectrum was taken from this mixture. Rh(acac)(CO)_2 (11 \mu mol, 2.6 mg) in DCM (1 ml) was injected via the injection chamber. The catalyst was left to incubate for one hour, during which spectra could be recorded. 1-Octene (2.1 mmol, 330 ml) in DCM (1 ml) was injected via the injection chamber, after which more spectra could be recorded.}


25 These simulations probably overestimate the rotation barrier, since the system is given only a limited time to respond to the sliding torsion perturbation. Increasing the temperature would give better sampling, but this also increases the temperature noise, making the measured barrier less accurate.