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

Ivo Jacobs, Adri C. T. van Duin, Arjan W. Kleij, Mark Kuil, Duncan M. Tooke, Anthony L. Spek and Joost N. H. Reek*

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)-based capsular 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. Since the 1990s, various research groups have investigated the application of such capsules as nanoreactors. A diversity of chemical processes, both stoichiometric and catalytic, has been carried out within molecular capsules. 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. Also the selectivity of a chemical process can be 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). 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(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. 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(salphen). These are easier to prepare than Zn(porphyrins), and can be structurally modified using modular approaches. 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)salphen. 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 metatripyridylphosphine 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&lt;sup&gt;b&lt;/sup&gt;</th>
<th>TOF&lt;sup&gt;c&lt;/sup&gt;</th>
<th>C1/C2</th>
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<td>1 + 2f</td>
<td>97</td>
<td>16</td>
<td>1.4</td>
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<sup>a</sup> This table is compiled from various sources (ref. 8 and 10). All experiments were performed at 25 °C in toluene, with a substrate/catalyst ratio of 1052. The reaction time was 73 h. See Table S1 (ESI) for more details.

<sup>b</sup> In percent.

<sup>c</sup> Average TOF in (mol aldehyde) (mol Rh)<sup>-1</sup> h<sup>-1</sup>, based on conversion.

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)salpens 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 Zn(salphen) complexes have selectivities significantly different from those obtained with the Zn(s)porphyrin capsule. There is obviously a difference in the steric impediment upon capsule formation using the various building blocks. Here we further investigated the conformational fluxionality of the capsule based on the smaller Zn(s)salphen building blocks, and the consequence in coordination chemistry and catalysis.

**Solid state structure**

The assembly 3b crystallized from a CH$_2$Cl$_2$–CH$_3$CN solution. Much to our surprise we found that the assembly exists in two different conformations, each being present in the unit cell. In one conformation all the pyridyl groups point up, so that the lone pairs of the pyridyl groups point in the same direction as that of the phosphorous center (designated as the “in” conformation). This causes the salphen units to encapsulate the phosphine (Fig. 1), similar to what molecular modelling suggested and what was found for the porphyrin encapsulated ligand. The other conformation has all the pyridyl groups pointing down (denoted as the “out” conformation), which makes the ligand very bulky, but the phosphorus donor atom is not encapsulated. It is clear that the capsule with the “in” conformation can only form monophosphine coordinated rhodium complexes, while in the “out” conformation maybe Rh–diphosphine complexes can be formed. In this way the conformation of the ligand directly influences the catalysis. It is also interesting to note that the conformation around zinc is different for the two complexes. In the “in” conformation the Zn ion resides 0.075(4) Å above the basal plane of the “close to square pyramidal” coordination environment around Zn

$\text{Table 4}$  Results of the rhodium catalysed hydroformylation of 1-octene with trispyridylphosphine and the building blocks illustrated in Scheme 1$^a$

<table>
<thead>
<tr>
<th>Entry</th>
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<th>TOF$^c$</th>
<th>C1/C2</th>
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<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.

$\text{Fig. 1}$  The molecular structure of the tris-meta-pyridylphosphine/3b assembly exhibits two conformations. Left the “in” conformation, right the “out” conformation, and below line drawings of the different conformations of the central part of the assembly. In light gray the salphen units and in dark grey the trispyridylphosphate template. Selected bond distances (Å) and angles (°) with esd’s in parentheses: P(1)–C(1) = 1.847(5), P(2)–C(38) = 1.827(4), Zn(1)–O(1) = 1.947(3), Zn(2)–O(3) = 1.971(3), Zn(1)–O(2) = 1.960(3), Zn(2)–O(4) = 1.959(3), Zn(1)–N(1) = 2.131(4), Zn(2)–N(4) = 2.114(3), Zn(1)–N(2) = 2.092(4), Zn(2)–N(5) = 2.071(3), Zn(1)–N(3) = 2.074(3), Zn(2)–N(6) = 2.105(3), C(1)–P(1)–C(1a) = 100.7(2), C(34)–P(2)–C(34c) = 103.3(2).

Ru(s)salphins as analogues for Zn(s)salphins

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 ($K_{\text{ass}} \sim 10^5$ M$^{-1}$). NMR analysis of the Zn(s)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(s)salphen
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 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{${^1}$H} 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 2g 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 similarity 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. 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) 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 to determine that complexes of type 3 most likely exist as multiple conformations both in solution and in the solid state. Whereas the porphyrin based assemblies were found in only one configuration in which the phosphorus donor atom was shielded by the porphyrins, the salphen based analogues can also adopt a conformation in which the phosphorus donor atom is much less shielded. The consequences for coordination chemistry are large, as for the porphyrins we found that the shielding resulted in exclusive mono-phosphorus coordination complexes, whereas for the salphen based assemblies bis-phosphorus complexes are also formed. Although in these complexes the metal is also shielded by the salphens, the activity and selectivity is very different from the encapsulated mono-phoshine rhodium complexes. Further exploration of the salphen framework might result in a structure that does share this ability with the porphyrins, although a valid question is whether this salphen would be as synthetically accessible as the easily prepared parent Zn(II)tetraphenylporphyrin. More interestingly, chiral versions of these salphen or porphyrin-based capsules are an attractive target for future directions in this area.

Notes and references

Hydroformylation experiments were performed in a stain-
less 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 con-
stant 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-tripryridylphosphine (9 eq.), Zn(salphen) (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.


Crystal structure determination of 3b: C₉₀H₁₀₂N₈O₄P₂Zn₃, F₃w = 1741.04, orange block, 0.22 × 0.2 × 0.14 mm³, trigonal
crystal system, space group P31c, cell parameters: a = 20.8644(4) Å, c = 52.9489(13) Å, V = 1996.18(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
DIRDIF,21 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 aniso-
tropic displacement parameters. H atoms were placed at
geoetically idealized positions [d(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 mol-
cules, which were taken into account by back-Fourier trans-
formation with PLATON/SQUEEZE,23 (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)² + (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.

14 V. Bocókić, A. Kalkan, M. Lutz, A. L. Spek, D. Gryko and
J. N. H. Reek, Submitted.


16 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,
M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr.,
T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam,
S. S. Iyengar, J. Tomasi, V. Barone, M. Cossi,
G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji,
M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa,
M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai,
M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross,
C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann,
O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli,
J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth,


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-meta-pyridylphosphine in d8-toluene was prepared, and measured. To this sample, 0.1 ml of a solution of Ru(II)salphen (0.375 mM) and tris-meta-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 \(P(\text{meta-pyr})_3\) (95 \(\mu\)mol, 25 mg) and ZnTPP (284 \(\mu\)mol, 192 mg) in DCM (13 ml) 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 \(\mu\)l) 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.