N2 fixation and dehydrogenation of methanol and formic acid with late transition metal complexes

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Citation for published version (APA):
Chapter 4

3-methylindole-based tripodal tetraphosphine ruthenium complexes in $\text{N}_2$ coordination and reduction and formic acid dehydrogenation
4.1 Introduction

As outlined in Chapter 1, electrocatalytic reduction reactions that store energy by the conversion of H\(^+\), CO\(_2\) or N\(_2\), are important reactions in the context of the transformation to a society based on sustainable energy. Therefore, the development of new catalysts that enable these reactions is needed. Homogeneous tripodal ligand transition metal complexes have shown beneficial reactivity over mono- or bidentate ligands in many organic transformations.\(^{[1-3]}\) In recent years, tripodal ligands coordinated to molybdenum, iron and cobalt were shown to be capable of the reduction of N\(_2\) to ammonia or silylamines.\(^{[4-10]}\) Also reversible hydrogen storage in CO\(_2\) was, among other complexes, shown to be possible with tripodal ligands coordinated to iron and cobalt.\(^{[11-13]}\) In Chapter 3 we reported the coordination of ligand L\(_1^H\) (Figure 1) to ruthenium. This ligand, which features three 1-(3-methylindolyl)diphenylphosphine groups tethered to a central phosphorus atom, stabilizes ruthenium in the oxidation states +2, +1 and 0. The isolated low oxidation state Ru\(^{II}\)Cl\(_2\)L\(_1^H\) and Ru\(^{II}\)N\(_2\)L\(_1^H\) complexes revealed interesting one-electron reactivity, as they were able to abstract chloride radicals from either chloroform or dichloromethane, leading to formation of the oxidized Ru\(^{III}\) parent complex. In this Chapter, we expand the coordination chemistry of ruthenium and 3-methylindole based ligands and investigate how the modification of the ligand scaffold and its electronic properties can influence the stability and activity of these complexes in dinitrogen coordination, reduction of dinitrogen and formic acid dehydrogenation. Ligand L\(_1^H\) was modified using functionalized P(PhR)\(_2\) units: a ligand with electron-withdrawing -CF\(_3\) groups (L\(_1^{CF_3}\)) and a ligand with electron-donating -OMe groups (L\(_1^{OMe}\)) in the para position of the phenyl rings were prepared (Figure 1). Additionally, the known structural isomer, L\(_2^H\) (Figure 2), in which the central P-donor is bound to the three nitrogen atoms of the 2-(3-methylindolyl)diphenylphosphine moiety, was also used in these studies.

4.2 Results and Discussion

Ligands L\(_1^H\) and L\(_2^H\) were prepared in two steps from 3-methylindole as described by van der Vlugt \textit{et al.}\(^{[14,15]}\) The new ligands L\(_1^{CF_3}\) and L\(_1^{OMe}\) were prepared in a similar way as L\(_1^H\), by reacting tris-2-(3-methylindolyl)phosphine\(^{[16]}\) with the corresponding chlorodiarylphosphine (Figure 1). The reaction of L\(_1^H\) with [RuCl\(_2\)benzene]\(_2\) in refluxing THF for 16 hours (see Chapter 3) led to the formation of the octahedral RuCl\(_2\)L\(_1^H\) complex in quantitative yield (Figure 2). Surprisingly, the other ligands did not react with [RuCl\(_2\)benzene]\(_2\) in refluxing THF.
Even after 36 hours only trace amounts of the target complexes were observed using ex situ $^{31}$P-NMR spectroscopy, and mainly the signals of the unreacted ligand were present. We next investigated if raising the reaction temperature would lead to the formation of the desired complexes and reacted the ligand with [RuCl$_2$ benzene]$_2$ in a refluxing THF/toluene (1:3) mixture set at 120 °C. The use of this solvent mixture at higher temperatures for 64 hours led to the formation of complexes RuCl$_2$L$_1^{CF3}$, RuCl$_2$L$_1^{OMe}$ and RuCl$_2$L$_2^H$ in >50 % isolated yields.

All three L$_1$-based RuCl$_2$L$_1$ complexes show similar $^{31}$P-NMR spectra: three signals in a ratio 1 (dt) : 2 (t): 1 (dt) (Figure 3). This splitting pattern indicates the formation
of a symmetric complex. Ruthenium(II) complexes tend to form 18 valence electron octahedral complexes, and in Chapter 3 it was already shown by X-ray analysis and NMR spectroscopy that complex RuCl$_2$L$_1^H$ indeed features an octahedral geometry with the two chlorides in mutual *cis* position and all four phosphines bound to the metal center. The above factors and the similarity of the $^{31}$P-NMR spectra of the other L$_1$-based complexes point to the same coordination behavior: an octahedral geometry around the metal center.

Layering of a dichloromethane solution of RuCl$_2$L$_1^{CF_3}$ with pentane resulted in the formation of crystals suitable for single crystal X-ray diffraction. The crystal structure (Figure 4) of RuCl$_2$L$_1^{CF_3}$ indeed shows an octahedral complex with the chlorides in *cis* position, which is in accordance with the observed $^{31}$P-NMR splitting pattern. The P$_1$-Ru-P$_2$ angle in RuCl$_2$L$_1^{CF_3}$ (157.78(6)°) is comparable to the one reported for the RuCl$_2$L$_1^H$ (160.04(3)°) complex (Table 1). The P$_1$–Ru, P$_2$–Ru and P$_3$–Ru bond distances all become slightly shorter in the RuCl$_2$L$_1^{CF_3}$ (2.3097(19) Å, 2.3445(19) Å and 2.2383(17) Å, respectively) compared to complex RuCl$_2$L$_1^H$ (2.3189(9) Å, 2.3727(9) Å and 2.2671(9) Å). The steric bulk of the –CF$_3$ groups clearly points away from the metal center, so steric effects do not play a significant role in the coordination chemistry. The averaged $c_s$ symmetry of the complex as indicated by $^{31}$P-NMR spectroscopy for both RuCl$_2$L$_1^H$ and RuCl$_2$L$_1^{CF_3}$ is not present in the solid state as two mirror images exist. This becomes evident when the symmetry equivalent molecules in the crystal structure of RuCl$_2$L$_1^{CF_3}$ are viewed from the bottom: the indolyl moieties either all point clockwise, or counterclockwise (Figure 5, showing the bottom view of RuCl$_2$L$_1^{CF_3}$ and a schematic representation). In solution, these two
mirror images rapidly interchange on the NMR timescale, resulting in one signal for the two trans phosphines. This is supported by the crystal structure as the methyl groups of the indolyl moiety do not seem to cause steric repulsion when interchanging from one to the other isomer. Despite several attempts, no crystals suitable for X-ray diffraction of the RuCl$_2$L$_1$OMe complex were obtained.

**Figure 4:** ORTEP drawing of RuCl$_2$L$_1$CF$_3$ (50% probability ellipsoids) showing one of the two rotamers. Solvent molecules and hydrogen atoms have been omitted for clarity.

**Figure 5:** Drawing of bottom view of RuCl$_2$L$_1$CF$_3$ of both isomers, showing only the 3-methylindolyl phosphine part. Insert: schematic representation of the two isomers where the 3-methylindolyl moiety is bend clockwise (left) or counterclockwise (right).
Interestingly, complex RuCl$_2$L$_2^H$ based on the structural isomer, L$_2^H$, displays a different $^{31}$P-NMR spectrum (Figure 6). The $^{31}$P-NMR spectrum of RuCl$_2$L$_2^H$ shows four signals each integrating for 1: two doublets of triplets and two doublets of doublets with an AX pattern indicating the formation of a complex with a different symmetry. Crystals obtained by layering of a DCM solution of this RuCl$_2$L$_2^H$ with pentane at 5 °C (Figure 7) were of sufficient quality to solve the solid state structure of complex RuCl$_2$L$_2^H$. This solid state structure helps to understand this AX pattern, as the bottom view displays much more steric hindrance around the central phosphorus atom P4 (see further).

Complexes RuCl$_2$L$_1^H$ (see Chapter 3) RuCl$_2$L$_1^{CF3}$ and RuCl$_2$L$_2^H$ all crystallize as a set of mirror images. In the solid state structure the $C_s$ symmetry is not present. This can be best observed when the symmetry-equivalent molecules are viewed from the bottom: the
indolyl moieties either point clockwise or counterclockwise, depending on the isomer (Figure 8). However, different than the L1-based complexes where the methyl groups are pointing towards the central phosphine, in complex RuCl₂L₂H the bulkier phenyl rings of the indolyl moiety point towards the central phosphine. From the crystal structure it seems that these phenyl rings have little space to flip to their other conformer and it therefore seems likely that this is associated with a high energy barrier in solution. As a result, the two phosphine atoms (P1 and P2, Figure 7) in trans position become inequivalent, leading to the observed AX pattern as a result of the P1–P2 coupling in the ³¹P-NMR spectrum.

Figure 7: ORTEP drawing of RuCl₂L₂H (50% probability ellipsoids) showing a side view of one of the two rotamers. Solvent molecules and hydrogen atoms have been omitted for clarity.

Figure 8: Bottom view of X-ray structure of RuCl₂L₂H of both isomers, showing only the 3-methylindolyl phosphine part. Insert: schematic representation of the two isomers where the 3-methylindolyl moiety is bend clockwise (left) or counterclockwise (right).
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The crystal structure of $\text{RuCl}_2\text{L}_2\text{H}^\text{II}$ further reveals minor differences in the coordination around the ruthenium center compared to $\text{RuCl}_2\text{L}_1\text{H}^\text{II}$ (Table 1). Where the $\text{P}1$–$\text{Ru}$, $\text{P}2$–$\text{Ru}$ and $\text{P}3$–$\text{Ru}$ bond distances become slightly longer ($2.3295(8)$ Å, $2.4079(8)$ and $2.2913(8)$ Å), the $\text{P}4$–$\text{Ru}$ bond distance ($2.1363(8)$ Å) decreases, pointing to a more π-acidic tris(amino)phosphine $\text{P}_4$ atom. The $\text{P}1$–$\text{Ru}1$–$\text{P}2$ angle is almost equal ($159.24(3)^\circ$) being closest to the theoretical $180^\circ$ of trans ligands in an ideal octahedral complex.

In Chapter 3 it was shown that two-electron-reduction of $\text{RuCl}_2\text{L}_1\text{H}^\text{II}$ under an $\text{N}_2$ atmosphere led to the formation of the $\text{RuN}_2\text{L}_1\text{H}^\text{II}$ complex, which features a characteristic infrared band corresponding to the coordinated $\text{N}_2$ at $\nu_{\text{N}_2} = 2125 \text{ cm}^{-1}$ (Table 2). To explore if the electronic properties of the ligands $\text{L}_1\text{CF}_3$, $\text{L}_1\text{OMe}$ and $\text{L}_2\text{H}$ have influence on the binding of $\text{N}_2$ to the corresponding ruthenium(0) complexes, these $\text{N}_2$ complexes were generated $\text{in situ}$ by reacting the ruthenium(II) complexes with two equivalents of $\text{KC}_8$ (Figure 9).

The extent of activation of the $\text{N}_2$ bond, which can be quantified by measuring the $\text{N}=\text{N}$ stretch frequency with infrared spectroscopy, is a direct measure for the extent of π-back-donation from the metal to the ligand, which is influenced by the ligand scaffold of the metal center. Table 2 shows the $\text{N}_2$ stretch frequencies of the $\text{Ru}^0\text{N}_2\text{L}$ complexes.

$\text{RuCl}_2\text{L}_1\text{R}$

$\text{L}_1\text{H}^\text{II}$, $\text{R} = \text{phenyl}$

$\text{L}_1\text{CF}_3$, $\text{R} = p$-$\text{phenyl-CF}_3$

$\text{L}_1\text{OMe}$, $\text{R} = p$-$\text{phenyl-OMe}$

$\text{RuCl}_2\text{L}_2\text{H}^\text{II}$

$\text{RuCl}_2\text{N}_2\text{H}^\text{II}$

**Figure 9:** Reaction of $\text{RuCl}_2\text{L}$ complexes with two equivalents of $\text{KC}_8$ in presence of $\text{N}_2$ forming the corresponding $\text{RuN}_2\text{L}$. 
As expected, the substitution of the para hydrogen atom of the PPh$_2$ moiety of L$^1$H with the electron-withdrawing –CF$_3$ group leads to a shift to higher frequencies in the infrared spectrum ($\nu_{N_2} = 2136$ cm$^{-1}$), as a result of weaker $\pi$-back-donation of the metal center of the RuN$_2$L$_1$CF$_3$ complex to the anti-bonding orbitals of the N$_2$ ligand. The electron-donating –OMe group leads to a shift of the IR signal towards lower frequencies ($\nu_{N_2} = 2113$ cm$^{-1}$), revealing stronger $\pi$-back-donation of the Ru(II) ion of the RuN$_2$L$_1$OMe complex to the anti-bonding orbitals of the N$_2$ ligand. Consequently, the peripheral phosphines induce measurable electronics effects on the d-orbitals of the ruthenium center; the phosphines cis to the N$_2$ ligand become stronger $\sigma$-donors and weaker $\pi$-acceptors for the L$^1$OMe and vice versa for L$^1$CF$_3$, which changes the binding properties of the N$_2$ ligand. Going from RuN$_2$L$_1$H ($\nu_{N_2} = 2125$ cm$^{-1}$) to the structural isomer RuN$_2$L$_2$H ($\nu_{N_2} = 2136$ cm$^{-1}$), the N$_2$ stretch frequency increases by 11 cm$^{-1}$. This is likely a result of the more $\pi$-acidic pivotal P-atom (atom P$_4$, Figure 10, top) of the tris(amino)phosphine donor ligand, which competes with the same metal d-orbitals of the metal as the N$_2$ ligand for $\pi$-back-donation interactions. Thus, substitution of the phosphine trans to the N$_2$ ligand for a more $\pi$-acidic group leads to weaker $\pi$-back-donation of the ruthenium center to the N$_2$ ligand. This indicates that the group trans to the N$_2$ molecule also has a direct effect on the electron-donating properties of the ruthenium metal. These results show that the electronics of the dinitrogen complexes can be tuned by ligand substitution, either by choosing electron-withdrawing or -donating substitutions on atoms in cis position or by changing the $\pi$-acidity of the atom in trans position.

In Chapter 3 it was already shown by X-ray diffraction analysis that the dinitrogen complex RuN$_2$L$_1$H possesses a trigonal bipyramidal geometry. Layering of a THF solution of RuN$_2$L$_1$CF$_3$ with pentane resulted in the formation of crystals suitable for X-ray diffraction (Figure 10). Similar to the RuN$_2$L$_1$H complex described in Chapter 3, RuN$_2$L$_1$CF$_3$ also shows a trigonal bipyramidal geometry. The N=N bond is slightly shorter in the RuN$_2$L$_1$CF$_3$ complex (1.064(5)Å) than for the RuN$_2$L$_1$H (1.085(5)Å) complex (Table 1), which is in accordance with the observed trend in the activation of the N$_2$ stretch frequency (Table 2) as a result of the induced electron-withdrawing –CF$_3$ groups. In solution, these complexes remain trigonal bipyramidal as judged from the $^{31}$P-NMR spectra that all show a doublet and a quartet.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_{N_2}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuN$_2$L$_1$CF$_3$</td>
<td>2136</td>
</tr>
<tr>
<td>RuN$_2$L$_1$H</td>
<td>2125</td>
</tr>
<tr>
<td>RuN$_2$L$_1$OMe</td>
<td>2113</td>
</tr>
<tr>
<td>RuN$_2$L$_2$H</td>
<td>2136</td>
</tr>
</tbody>
</table>

Table 2: IR frequency of the selected RuN$_2$L complexes.
The dinitrogen ligand in all of these ruthenium complexes is weakly coordinating as judged by the relatively small shift in the infrared stretching frequency signals as compared to that of free N₂ (νₙ₂ = 2359 cm⁻¹) (Table 2). This suggests that the dinitrogen ligand can be replaced easily and dinitrogen reduction to ammonia may not be feasible, as the competitive hydrogen evolution reaction may proceed much faster (see Chapter 1), which is likely the reason that no ammonia was detected when complex RuCl₂L₁H was subjected to excess reductant and protons (see Chapter 3). Interestingly, Nishibayashi has shown that Ru₃(CO)₁₂ is capable of mediating the reduction of dinitrogen with chlorotrimethylsilane.

Figure 10: ORTEP drawing of RuN₂L₁⁺ (top) and RuN₂L₁⁻ (bottom) (50% probability ellipsoids) showing one of the two rotamers. Solvent molecules and hydrogen atoms have been omitted for clarity.
in presence of potassium graphite, forming 6 equiv. of tris(trimethylsilyl)amine.\(^{[17]}\) This latter dinitrogen reduction reaction is based on a different mechanism, and does not suffer from hydrogen evolution competition. Therefore, we set to explore the reactivity of the tripodal tetraphosphine ruthenium(II) complexes in the dinitrogen reduction reaction with chlorosilanes (Figure 11).

\[
\text{N}_2 + \text{KC}_8 (100 \text{ eq}) + \text{Me}_3\text{SiCl} (100 \text{ eq}) \rightarrow (\text{Me}_3\text{Si})_3\text{N} \\
\text{THF, rt}
\]

Figure 11: Reduction of dinitrogen with KC\(_8\) Me\(_3\)SiCl and RuCl\(_2\)L forming (Me\(_3\)Si)_3N.

A mixture of the RuCl\(_2\)L\(_1\) complexes with 100 equiv. of KC\(_8\) and 100 equiv. of chlorotrimethylsilane in 10 mL THF at room temperature under an atmosphere of dinitrogen was stirred for 1 day after which an aliquot of the reaction mixture was analyzed using GC for its tris(trimethylsilyl)amine content. Modest yields of \(~1.5\) equivalents of (TMS)\(_3\)N were detected, regardless of the complex used (Table 3). The use of metallic sodium as reductant or longer reaction times did not increase the overall yield.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Equiv. (TMS)(_3)N(^{[a]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuCl(_2)L(_1)CF(_3)</td>
<td>0.92(^{[b]})</td>
</tr>
<tr>
<td>RuCl(_2)L(_1)H</td>
<td>1.83(^{[b]})</td>
</tr>
<tr>
<td>RuCl(_2)L(_1)OMe</td>
<td>1.74(^{[b]})</td>
</tr>
<tr>
<td>RuCl(_2)L(_2)H</td>
<td>1.40(^{[b]})</td>
</tr>
<tr>
<td>[RuCl(_2)benzene](_2)</td>
<td>1.29(^{[c]})</td>
</tr>
</tbody>
</table>

Table 3: Formation of (Me\(_3\)Si)_3N with RuCl\(_2\)L complexes.

\(^{[a]}\) Conditions: \(~33\) µmol of the complex was suspended together with KC\(_8\) (100 equiv.) in 10 mL THF after which the chlorotrimethylsilane (100 equiv.) was added. The suspension was stirred for 23 hours at room temperature. \(^{[b]}\) Average of two runs. \(^{[c]}\) Equivalents per ruthenium atom.

To gain more insight in the nitrogen reduction reaction using these novel ruthenium complexes, the reduction reaction was followed in time for complexes RuCl\(_2\)L\(_1\)H and RuCl\(_2\)L\(_2\)H, analyzing an aliquot of the reaction mixture every hour. The reaction profile shows an incubation period of 1 hour after which product formation gradually increases (Figure 12). Such an incubation period was also observed for various iron and cobalt systems that were investigated for dinitrogen reduction under comparable conditions (see Chapter 1)\(^{[17–19]}\), leading to similar activities in the formation of tris(trimethylsilyl)amine regardless of the initial catalyst structure. These literature experiments suggest that the
active species are being formed via initial ligand dissociation from the iron and cobalt pre-catalysts. The nature of the reported catalysts could not be elucidated, as no dinitrogen containing species could be detected. Formation of nanoparticles/metabolic precipitation also did not seem to play a role in these systems that were reported in literature, as no different reactivity was observed upon mercury poisoning of the catalysis.

A similar behavior may also occur for our complexes; where the incubation period leads to the same species for all catalysts, regardless of which ligand is coordinated to ruthenium. This finding would also be in line with the absence of major electronic effects of the various complexes used. To test this hypothesis, we performed a catalytic reaction with \([\text{RuCl}_2\text{benzene}]_2\) in the absence of the tripodal indolyl-phosphine ligand. When \([\text{RuCl}_2\text{benzene}]_2\) was subjected to the same reaction conditions, again comparable amounts (1.29 equiv.) of silylamine were formed per ruthenium atom, which indeed shows that the ligand does not affect the conversion of dinitrogen. Apparently, the ligand scaffold does not protect the metal center sufficiently to prevent metal dissociation under the strongly reducing conditions used in this dinitrogen reduction reaction.

Next, we studied if these complexes were active in the formic acid dehydrogenation reaction (Figure 13).

Formic acid dehydrogenation proceeds faster with electron-rich ruthenium centers as was shown by Himeda et al. He used a series of bipyridine ligands with various
substituents at the \textit{para} position (\(-\text{O}^-, \text{-OMe}, \text{-Me, -CO}_2\text{, and -H}\)). From the activity of the ruthenium complexes based on these bipyridine ligands, it was concluded that electron-rich complexes were better formic acid dehydrogenation catalysts, giving rise to higher turnover frequencies. The tripodal tetraphosphine ruthenium complexes presented in this Chapter are also based on ligands with different electronic properties. We anticipated that the modifications that we made to these ligands could influence the reactivity of the corresponding complexes in the formic acid dehydrogenation reaction. The RuCl\textsubscript{2} \textit{L} complexes are coordinatively saturated, which made abstraction of the chloride atoms necessary in order to arrive at active complexes. Therefore, we preactivated the complexes by stirring them with silver tetrafluoroborate (2 equiv.) in THF for 2 hours and used the filtered solutions for the catalytic reactions. Upon addition of formic acid to a refluxing solution of such a complex in tetrahydrofuran, gas production started within 1-5 minutes. The reactions were monitored volumetrically with a gas burette (see experimental section for a schematic representation). A typical time profile of the dehydrogenation reaction with catalyst RuCl\textsubscript{2} \textit{L1OMe} is demonstrated in Figure 14. The overall results of the different catalysts used in the dehydrogenation of formic acid are presented in Table 4. The gas outlet was analyzed using gas chromatography, which confirmed presence of both carbon dioxide and dihydrogen. No traces of carbon monoxide were detected.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure14.png}
\caption{Hydrogen evolution from formic acid with catalyst RuCl\textsubscript{2} \textit{L1OMe} as detected volumetrically with a gas burette.}
\end{figure}
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Complexes RuCl$_2$L$_1^{\text{Ome}}$, RuCl$_2$L$_1^{\text{H}}$, and RuCl$_2$L$_2^{\text{H}}$ follow the same trend as what Himeda already noticed: the most electron-rich complex RuCl$_2$L$_1^{\text{Ome}}$ has the highest activity (TOF = 121 h$^{-1}$) followed by RuCl$_2$L$_1^{\text{H}}$ (TOF = 76 h$^{-1}$) and the least electron-rich RuCl$_2$L$_2^{\text{H}}$ (TOF = 33 h$^{-1}$). Interestingly, the RuCl$_2$L$_1^{\text{CF3}}$ complex (TOF = 124 h$^{-1}$) shows a comparable, even slightly higher activity as the electron-rich RuCl$_2$L$_1^{\text{Ome}}$ complex. The reason for this unusual observation is currently not clear. The TOFs found for the RuCl$_2$L complexes in the formic acid decomposition reaction are relatively low compared to examples of the group of Li, who reported a TOF of 487500 h$^{-1}$ with [Cp*Ir(L1)Cl]Cl (L1 = 2,2'-bi-2-imidazoline) in neat HCOOH at 90°C$^{[21]}$, the group of Grützmacher who reported the [K(dme)$_2$][RuH(trop$_2$dad)] (trop$_2$dad = 1,4-bis(5H-dibenzo[a,d]cyclohepten-5-yl)-1,4-diazabuta-1,3-diene) complex that reached TOF's of 24000 h$^{-1}$ in boiling HCOOH/dioxane$^{[22]}$ and the group of Gonsalvi who demonstrated TOF's of up to 4556 h$^{-1}$ with the more related Ru(H)$_2$(P4) complexes (P4 = meso-1,1,4,7,10-hexaphenyl-1,4,7,10-tetraphosphadecane) in HCOOH/N,N-dimethyloctylamine/propylene carbonate mixtures at 80 °C$^{[23]}$. These initial results show that the complexes are active in the dehydrogenation of formic acid and that different reactivity is observed upon ligand modification. Further reactivity studies with these complexes should be performed to elucidate the mechanism of the reaction and to find the maximum capacities (stability, temperature, solvent) of these catalysts.

4.3 Conclusions

In conclusion, we have shown the formation of new ruthenium complexes based on a tripodal 3-methylindolephosphine scaffold. The ligand has two structural isomers, where one of those isomers was substituted with electron-withdrawing and -donating groups.
These ligands were successfully coordinated to \([\text{RuCl}_2\text{benzene}]_2\) leading to the formation of octahedral complexes with the two chlorides in \(cis\) position. The stoichiometric reduction of these complexes yielded the corresponding dinitrogen complexes, where electronic effects in the \(\text{N}=\text{N}\) stretch frequency were observed as a result of the ligand modifications. The complexes were studied in the dinitrogen reduction reaction with chlorosilanes and \(\text{KC}_8\), yielding stoichiometric amounts of the silylamines. When the reaction was followed in time, an incubation period was observed. This incubation period in combination with the similar activities found for all of these complexes may hint at the formation of the same active catalyst in all of the catalytic reactions, regardless of the initial structure. Thus, it seems that the ligand is not able to effectively protect the metal from dissociation under these highly reducing conditions. The complexes were also studied in the formic acid dehydrogenation reaction. Activities between \(\text{TOF} = 33\) and \(124\) \(\text{h}^{-1}\) were reached depending on the ligand used. This finding shows that the modification of the ligand can influence the rate of the formic acid dehydrogenation reaction under the conditions used. Further studies with these complexes should be performed to elucidate the reaction mechanism and stability of the catalysts.

4.4 Experimental section

General methods

All reactions were carried out under an atmosphere of nitrogen or argon using standard Schlenk techniques or in the glovebox. Reagents were purchased from commercial suppliers and used without further purification. THF, pentane, hexane and \(\text{Et}_2\text{O}\) were distilled from sodium benzophenone ketyl. These solvents were degassed using the freeze-pump-thaw method (three cycles) and stored under dinitrogen atmosphere. \(\text{CH}_2\text{Cl}_2\) was distilled from \(\text{CaH}_2\) under dinitrogen. NMR spectra (\(\text{1H}, \text{31P},\) and \(\text{13C}\{\text{1H}, \text{31P}\}\)) were measured on a Bruker DRX 500, Bruker AV 400, Bruker DRX 300 or on a Bruker AV 300 spectrometer. IR spectra (ATR mode) were recorded with a Bruker Alpha-p FT-IR spectrometer. High resolution mass spectra were recorded on a JEOL AccuTOF LC, JMS-T100LP mass spectrometer using cold electron-spray ionization (CSI) at -40 °C. GC measurements were performed on a Shimadzu GC-17A Gas Chromatograph (Shimadzu Corporation, Kyoto, Japan) with a Supelco SPB-1 fused silica capillary column. Tris-2-(3-methylindolyl)phosphine\(^{[14]}\), \(\text{L}_1\text{H}^{[14]}\), \(\text{L}_2\text{H}^{[14]}\) and potassium graphite (\(\text{KC}_8\))\(^{[24]}\) were prepared according to literature procedures. Chlorobis[4-(trifluoromethyl)phenyl]phosphine (Alfa Aesar) and chlorobis[4-methoxyphenyl]phosphine (Sigma Aldrich) are commercially available chemicals and were used without further purification.
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Synthesis of compounds

Tris-2-(3-methyl-N-di[4-(trifluoromethyl)phenyl]phosphinoindolyl)phosphine (L1\textsubscript{CF3}) was prepared in the same way as L1\textsubscript{H} using chlorobis[4-(trifluoromethyl)phenyl]phosphine: To a solution of tris-2-(3-methylindolyl)phosphine (1.9 g, 4.53 mmol) in THF (50 mL) was added n-BuLi (2.5 M in hexanes, 5.7 mL, 14.3 mmol) at -78 °C. The resulting solution was stirred for 1 h and chlorobis[4-(trifluoromethyl)phenyl]phosphine (3.5 mL, 14.0 mmol) was added. The reaction mixture was stirred for 16 h allowing to warm slowly to room temperature. The resulting suspension was concentrated in vacuo, redissolved in CH\textsubscript{2}Cl\textsubscript{2} (total amount of 50 mL including washing of the pads), filtered through a pad of basic alumina and subsequently through a pad of SiO\textsubscript{2}. The solvent was removed under reduced pressure and resulting in a yellow foam. This yellow foam was purified by SiO\textsubscript{2} chromatography using a gradient from pure hexane to 2% Et\textsubscript{2}O in hexane. Yield: 2.66 g (42%).

\[ ^1H\text{-NMR} (300 MHz CDCl}_3): \delta: 7.44 (d, J = 8.6 Hz, 15H), 7.33 – 7.22 (m, 6H), 7.21 – 7.14 (m, 6H), 7.11 (t, J = 7.6 Hz, 3H), 6.93 (t, J = 7.8 Hz, 3H), 6.59 (d, J = 8.4 Hz, 3H), 2.14 (s, 9H). \]

\[ ^19F\text{-NMR} (282 MHz, CDCl}_3): \delta = -60.78 \text{ ppm}. \]

\[ ^31P\text{-NMR} (121 MHz, CDCl}_3): \delta: 32.63 (d, J = 151.2 Hz, 3P), -76.09 (q, J = 151.6 Hz, 1P). \]

\[ ^{13}C\{^1H, ^{31}P\}\text{-NMR} (75 MHz, (CDCl}_3): \delta: 114.02, 140.13, 139.77, 139.53, 139.36, 133.67, 131.91, 131.71, 131.62, 131.43, 129.27, 125.60, 125.53, 125.42, 125.33, 123.72, 122.00, 121.21, 119.50, 113.97, 9.94 \text{ ppm}. \]

Tris-2-(3-methyl-N-di[4-methoxyphenyl]phosphinoindolyl)phosphine (L1\textsubscript{OMe}) was prepared in the same way as L1\textsubscript{H} using chlorobis[4-methoxyphenyl]phosphine: To a solution of tris-2-(3-methylindolyl)phosphine (2.20 g, 5.22 mmol) in THF (50 mL) was added n-BuLi (2.5 M in hexanes, 6.6 mL, 16.44 mmol) at -78 °C. The resulting solution was stirred for 1 h and chlorobis[4-methoxyphenyl]phosphine (4.83 g, 17.23 mmol) dissolved in 10 mL THF was added. The reaction mixture was stirred for 3 days allowing to warm to room temperature. The resulting suspension was concentrated in vacuo, redissolved in CH\textsubscript{2}Cl\textsubscript{2} (total amount of 50 mL including washing of the pads), filtered through a pad of basic alumina. Evaporation of the solvent and trituration with Et\textsubscript{2}O yielded a white solid which was recrystallized from vapour diffusion evaporation of Et\textsubscript{2}O to a concentrated THF solution. Washing with Et\textsubscript{2}O and drying under vacuum yielded the ligand in pure form. Yield: 4.03 g (67%).

\[ ^1H\text{-NMR} (300 MHz, (CD\textsubscript{3})_2CO): \delta: 7.46 (d, J = 7.9, 1.0 Hz, 3H), 7.39 – 7.27 (m, 6H), 7.20 – 7.07 (m, 6H), 7.05 – 6.95 (t, 3H), 6.94 – 6.81 (m, 12H), 6.77 (d, 6H), 3.74 (s, 18H), 2.01 (s, 9H) ppm. \]

\[ ^31P\text{-NMR} (122 MHz, (CD\textsubscript{3})_2CO): \delta: 36.83 (d, J = 166.0 Hz, 3P), -76.21 (q, J = 166.7, 1P) ppm. \]

\[ ^{13}C\{^1H, ^{31}P\}\text{-NMR} (75 MHz, (CD\textsubscript{3})_2CO): \delta: \]
Chapter 4

161.42, 141.33, 141.16, 134.63, 134.33, 134.06, 134.03, 127.95, 127.78, 127.58, 127.38, 124.22, 123.07, 120.83, 119.56, 115.06, 114.91, 114.86, 114.81, 114.77, 55.52, 9.87 ppm.

**RuCl$_2$L$_1$:** L$_1$ (1.3732 g, 0.99 mmol) and [RuCl$_2$(C$_6$H$_6$)$_2$] (249.3 mg, 0.50 mmol) were suspended in THF (4 mL) and toluene (8 mL) and stirred at 60 °C for 64 h. After cooling, the yellow precipitated complex was filtered, washed with toluene (1 x 2 mL) and pentane (3 x 3 mL) and dried overnight in the vacuum oven at 40 °C. Yield: 0.9914 g (64 %) of a yellow solid. Recrystallization of the complex by layering a DCM solution with pentane at 5 °C gave crystals suitable for X-ray diffraction analysis. **'H-NMR (300 MHz, CDCl$_3$):** δ 7.72 (dd, J = 10.8, 8.0 Hz, 3H), 7.59 (dt, J = 10.5, 5.3 Hz, 4H), 7.53 – 7.31 (m, 8H), 7.24 (t, J = 7.6 Hz, 4H), 7.18 – 7.01 (m, 7H), 6.99 – 6.81 (m, 7H), 6.11 (d, J = 8.5 Hz, 2H), 5.86 (d, J = 8.5 Hz, 1H), 2.93 (s, 6H), 2.69 (s, 3H) ppm.

**31P-NMR (121 MHz, CDCl$_3$):** δ 99.83 (dt, J = 31.5, 26.4 Hz, 1P), 78.90 (t, J = 26.3 Hz, 2P), 49.00 (dt, J = 30.3, 26.7 Hz, 1P) ppm. **13C{1H,31P}-NMR (75 MHz, CDCl$_3$):** δ 134.83, 134.73, 133.95, 133.82, 132.74, 132.63, 132.31, 132.18, 131.43, 131.31, 129.54, 128.96, 128.73, 128.49, 128.49, 128.05, 128.03, 127.88, 127.74, 127.68, 127.58, 127.44, 126.91, 126.76, 126.44, 126.30, 125.15, 124.71, 124.64, 122.90, 122.45, 122.32, 120.76, 120.22, 117.80, 115.44, 115.00, 13.64, 12.27, 11.99 ppm. **Mass Analysis (CSI)** [C$_{69}$H$_{45}$Cl$_1$F$_{18}$N$_3$P$_4$Ru]$^+$: calc: 1518.1024 found 1518.1067.

**RuCl$_2$L$_1$:** L$_1$ (1.02 g, 0.88 mmol) and [RuCl$_2$(C$_6$H$_6$)$_2$] (227.9 mg, 0.45 mmol) were suspended in THF (4 mL) and toluene (8 mL) and stirred at 120 °C for 3 days leaving a pale brown solution. Upon cooling of the reaction mixture an off white solid precipitated. This solid was filtered and washed with hexane (3 x 3 mL) and dried overnight in the vacuum oven at 40 °C resulting in the product as a brown-white solid. Yield: 1.15 g of an off white solid (97.8 %). **'H-NMR (300 MHz, CDCl$_3$):** δ 7.66 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 7.9 Hz, 1H), 7.44 – 7.32 (m, 4H), 7.32 – 7.24 (m, 1H), 7.24 – 7.02 (m, 10H), 6.89 (q, J = 7.8, 6.9 Hz, 4H), 6.77 (t, J = 7.8 Hz, 1H), 6.68 (d, J = 8.5 Hz, 4H), 6.28 (d, J = 8.5 Hz, 2H), 6.24 (d, J = 7.9 Hz, 2H), 6.12 (d, J = 8.5 Hz, 4H), 5.90 (d, J = 8.5 Hz, 1H), 3.70 (d, J = 1.8 Hz, 12H), 3.62 (s, 6H), 2.84 (s, 6H), 2.60 (s, 3H) ppm. **31P-NMR (121 MHz, CDCl$_3$):** δ 107.24 (dt, J = 32.0, 26.0 Hz, 1P), 83.78 (t, J = 26.6 Hz, 2P), 54.51 (dt, J = 30.9, 26.9 Hz, 1P) ppm. **13C{1H,31P}-NMR (75 MHz, CDCl$_3$):** δ = 159.95, 159.46, 139.85, 139.70, 135.39, 135.35, 135.27, 133.02, 132.98, 132.86, 123.72, 123.69, 121.47, 121.27, 120.20, 117.09, 113.38, 113.29, 112.88, 112.72, 112.03, 111.96, 111.89, 77.43, 77.00, 76.58, 54.90, 54.82, 54.79, 11.92, 11.68 ppm. **Mass Analysis (CSI)** [C$_{69}$H$_{63}$Cl$_1$F$_{18}$N$_3$O$_6$P$_4$Ru]$^+$: calc: 1290.2399 found 1290.2400.
RuCl$_2$L$_2$: L$_2$ (587.3 mg, 0.60 mmol) and [RuCl$_2$(C$_6$H$_6$)]$_2$ (150.1 mg, 0.30 mmol) were suspended in THF (3 mL) and toluene (6 mL) and stirred at 120 °C for 64 h. After cooling, 20 mL of hexane was added, which resulted in the precipitation of a yellow solid. The solid was filtered, washed hexane (3 x 3 mL) and dried overnight in the vacuum oven at 60 °C. Yield: 477.5 mg (69.1%) of a yellow solid.

Recrystallization of the complex by layering a DCM solution with pentane at 5 °C gave crystals suitable for X-ray diffraction analysis.

1H-NMR (300 MHz, CDCl$_3$): δ 7.90 (dd, J = 11.6, 7.7 Hz, 2H), 7.84 – 7.65 (m, 6H), 7.60 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 9.3 Hz, 3H), 7.45 (d, J = 7.8 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.32 – 7.12 (m, 9H), 7.11 – 6.92 (m, 6H), 6.90 – 6.75 (m, 7H), 6.70 (d, J = 8.4 Hz, 1H), 6.36 (t, J = 8.4 Hz, 3H), 6.23 (dd, J = 7.5 Hz, 2H), 1.97 (s, 3H), 1.72 (s, 3H), 1.40 (s, 3H) ppm.

31P-NMR (121 MHz, CDCl$_3$): δ 144.43 (dt, J = 38.9, 37.8 Hz, 1P), 39.22 (dt, J = 45.0, 23.6 Hz, 1P), 24.70 (ddd, J = 331.4, 39.7, 25.6 Hz, 1P) ppm.

13C{1H,31P}-NMR (75 MHz, CDCl$_3$): δ 134.83, 134.73, 133.95, 133.82, 132.74, 132.63, 132.31, 132.18, 131.43, 131.31, 129.54, 128.73, 128.49, 128.18, 128.05, 127.88, 127.74, 127.68, 127.58, 127.44, 126.91, 126.76, 126.44, 126.31, 125.15, 124.71, 124.64, 122.90, 122.45, 122.32, 120.76, 120.22, 117.80, 115.44, 115.00, 13.64, 12.27, 11.99 ppm.

Mass Analysis (CSI) [C$_6$$_3$H$_{51}$ClN$_3$P$_4$Ru]$: calc: 1110.1789; found: 1110.1779.

Reduction of RuCl$_2$L to RuN$_2$L
RuCl$_2$.L ($\pm$ 17 µmol) and KC$_8$ (2-3 equiv.) were transferred to flame dried Schlenk flask in the glovebox. THF (2 mL) was added and the suspension was stirred for two to three hours, after filtration a red solution was obtained. Part of this solution was used for in-situ infrared spectrometry, part of the solution was used for in-situ 31P-NMR analysis and the rest of the solution was set for crystallisation via slow diffusion evaporation of pentane. RuCl$_2$.L$_1$OMe resulted in a purple solution after filtration, which did not show an infrared band after two hours. However, after one day, the solution turned more red and the corresponding infrared band could be detected. The infrared analysis yielded the corresponding infrared bands as given in Table 2. The 31P-NMR analysis showed presence of one doublet and one quarted, indicative for a symmetrical compound, which corresponds with the proposed trigonal bipyramidal geometry. The crystallisation yielded crystals for the RuCl$_2$.L$_1$H (Chapter 3) and the RuCl$_2$.L$_1$OMe, which are discussed in the paper.

Catalysis: dinitrogen reduction
The catalyst (33 µmol) and KC$_8$ (100 equiv) were transferred to a 100-mL flame dried Schlenk flask equipped with a glass stirring bean in the glovebox. 10 mL of dry THF was added, followed by the addition of the chlorotrimethylsilane (100 equiv.).
The suspension was stirred overnight. 10 µL of \( n \)-decane was added as internal standard, after which a filtered aliquot of the reaction mixture was measured on the Gas-GC.

**Catalysis in time: dinitrogen reduction**

The same procedure as for the normal nitrogen reduction was used, adding the 10 µL of \( n \)-decane right away and taking an filtered aliquot of the reaction mixture every hour, which was subsequently measured on the Gas-GC.

**Catalysis: Formic acid dehydrogenation**

Hydrogen evolution was initiated by the addition of formic acid (0.4 M) to a refluxing catalyst (± 8.5 µmol) solution in THF (3 mL) in a 10-mL reaction flask equipped with a condenser. The gas was cooled via a condenser, which outlet was connected to a burette filled with water (Figure 15). The displacement of the water level in the buret was measured in time. The second burette was also filled with water and used to compensate for pressure build up keeping the water levels at equal height. TOF\(_{H2} \) was calculated using equation 1.\[^{[25]}\]

\[
TOF_{H2} = \frac{V_{obs} \times 0.5}{V_m \times n_{cat}}
\]  

(4.1)

\( V_{obs} \): measured gas volume displacement cylinder [mL]  
\( V_m \): molar gas volume: 24.49 [mL/mmol]  
\( n_{cat} \): amount of catalyst [mmol]

**Figure 15:** Hydrogen evolution set up.
**X-ray diffraction analysis**

Crystallographic data was obtained using a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator. The intensities were integrated with the SAINT software package.\textsuperscript{[26]} Multiscan absorption correction and scaling was performed with SADABS.\textsuperscript{[27]} The structure was solved with Intrinsic Phasing Methods using SHELXT.\textsuperscript{[28]} Least-squares refinement was performed with SHELXL 2013\textsuperscript{[29]} against $F^2$ of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. All structures have solvent accessible voids filled with disordered solvent. Their contribution to the structure factors in the refinement was taken into account with the PLATON/SQUEEZE approach.\textsuperscript{[30]}

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**Tabel 4:** Duplo measurements for formic acid dehydrogenation by the depicted catalysts.

<table>
<thead>
<tr>
<th>Complex</th>
<th>TOF (h(^{-1})) #1</th>
<th>TOF (h(^{-1})) #2</th>
<th>TOF (h(^{-1})) average</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuCl(_2)L(<em>1)(</em>{CF3})</td>
<td>120.8</td>
<td>127.2</td>
<td>124</td>
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<tr>
<td>RuCl(_2)L(<em>1)(</em>{H})</td>
<td>79.3</td>
<td>71.9</td>
<td>75.6</td>
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<tr>
<td>RuCl(_2)L(<em>1)(</em>{OMe})</td>
<td>23.5</td>
<td>117.4</td>
<td>120.5</td>
</tr>
<tr>
<td>RuCl(_2)L(<em>2)(</em>{H})</td>
<td>22.4</td>
<td>42.7</td>
<td>32.6</td>
</tr>
</tbody>
</table>
Table 5: Crystallographic data for RuCl$_2$L$_1^{CF3}$, RuCl$_2$L$_2^H$ and RuN$_2$L$_1^H$.

<table>
<thead>
<tr>
<th>Complex</th>
<th>RuCl$_2$L$_1^{CF3}$</th>
<th>RuCl$_2$L$_2^H$</th>
<th>RuN$_2$L$_1^{CF3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{69}$H$</em>{45}$Cl$_{18}$N$_3$P$_4$Ru + solvent</td>
<td>C$<em>{63}$H$</em>{51}$Cl$_{2}$N$_3$P$_4$Ru, 2(CH$_2$Cl)$_2$ + solvent</td>
<td>C$<em>{45}$H$</em>{45}$F$_{18}$N$_5$P$_4$Ru + solvent</td>
</tr>
<tr>
<td>FW</td>
<td>1553.93$^a$</td>
<td>1315.77$^a$</td>
<td>1511.05$^a$</td>
</tr>
<tr>
<td>Temperature [K]</td>
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<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Radiation</td>
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<td>Mo K$\alpha$</td>
<td>Mo K$\alpha$</td>
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<tr>
<td>Wavelength [Å]</td>
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<td>0.71073</td>
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<td>Cryst syst</td>
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<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C 2/c</td>
<td>P 21/n</td>
<td>P 21/c</td>
</tr>
<tr>
<td>a [Å]</td>
<td>21.594(3)</td>
<td>19.1879(9)</td>
<td>14.2851(6)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>27.753(4)</td>
<td>18.1604(8)</td>
<td>18.9090(8)</td>
</tr>
<tr>
<td>c [Å]</td>
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<td>19.7879(9)</td>
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</tr>
<tr>
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</tr>
<tr>
<td>$\beta$ [deg]</td>
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<td>97.011(2)</td>
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<tr>
<td>$\gamma$ [deg]</td>
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<td>90</td>
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<tr>
<td>Volume [Å$^3$]</td>
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<tr>
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<td>26.450</td>
</tr>
<tr>
<td>Density [Mg m$^{-3}$]</td>
<td>1.442$^a$</td>
<td>1.268$^a$</td>
<td>1.253$^a$</td>
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<tr>
<td>Absorp. Coeff. [mm$^{-1}$]</td>
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<td>0.591$^a$</td>
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<tr>
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<td>3040$^a$</td>
</tr>
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<td>0.1435/</td>
<td>0.2002/</td>
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<tr>
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<td>1.436</td>
</tr>
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</table>

a) Excluding the disordered solvent contribution.

4.5 References