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

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Chapter 3

Metallo-radical reactivity of an 3-methylindole-based tripodal PP₃ ruthenium(+I) complex and its ruthenium(0) analogue
3.1 Introduction

Metals of the 4d and 5d row of the periodic table, and especially late transition metals in low oxidation states, strongly prefer closed-shell 18 valence electron configurations.\[^{[1]}\] As a result, complexes of such metals that possess an open-shell electronic structure with an odd-electron d-orbital configuration are rare, and have a strong tendency to undergo reactions producing closed-shell products. Such ‘metallo-radicals’ undergo a variety of highly interesting bond-activation processes, such as hydrogen atom abstraction from C–H bonds, binuclear C–H splitting between two metallo-radicals, C–C bond activation, radical-type C–N, C–O and C–X bond activation, (reversible) M–M bond formation, single-electron reductive coupling of carbon monoxide and olefins, and ligand-ligand coupling processes.\[^{[2,3]}\] Transient metallo-radicals are also frequently involved in oxidatively or reductively induced reductive elimination and oxidative addition reactions,\[^{[2]}\] and play an important role in a variety of transition metal controlled radical processes such as photoredox catalysis.\[^{[4]}\] Inspired by these intriguing examples, we wondered if we could access and isolate stable metallo-radical ruthenium(+I) complexes in a rigid tripodal PP\(_3\)-ligand environment for subsequent reactivity evaluation. As low-valent ruthenium complexes in general are typically quite reactive, we also targeted the synthesis of related PP\(_3\)-ligand ruthenium(0) complexes in our studies.

Ru\(^{\text{I}}\) metallo-radical complexes in general are very rare,\[^{[5–10]}\] and so far, only two types of Ru\(^{\text{I}}\) complexes have been successfully isolated. The first isolated Ru\(^{\text{I}}\) complex was reported by the group of Peters.\[^{[11]}\] This complex features an anionic σ-donating (SiP\(_{\text{iPr}}\)\(_3\))\(^−\) (SiP\(_{\text{iPr}}\)\(_3\) = (2-\text{iPr}\(_2\)PC\(_6\)H\(_4\))\(_3\)Si) ligand, which stabilizes the ruthenium metal center in oxidation states ranging from +III to 0. The reduction potentials that were found for these complexes in THF are −1.24 V vs Fc/Fc\(^+\) for the Ru\(^{\text{II}}\)/Ru\(^{\text{I}}\) couple and −2.14 V vs Fc/Fc\(^+\) for the Ru\(^{\text{I}}\)/Ru\(^\text{0}\) couple. These reductions were also performed chemically with stoichiometric amounts of KC\(_8\), yielding the targeted oxidation states. The five-coordinate 17-valence electron ruthenium(+I) complex (SiP\(_{\text{iPr}}\)\(_3\))Ru\(^{\text{I}}\)N\(_2\) was successfully isolated and characterized in the solid state by X-ray diffraction analysis, showing a substantially distorted trigonal bipyramidal geometry. In addition, complex (SiP\(_{\text{iPr}}\)\(_3\))Ru\(^{\text{I}}\)N\(_2\) was shown to react with organic azides to (catalytically) form N-coupled azoarenes as products.\[^{[12]}\]

The other isolated ruthenium(+I) complex was recently published by the group of Grützmacher.\[^{[13]}\] The ruthenium complex consists of two bidentate π-accepting tropPPh\(_2\) (trop = 5H-dibenzo[a,d]cyclohepten-5-yl) ligands, which form stable ruthenium complexes in the oxidation states ranging from +II to 0. These oxidation states could also be accessed electrochemically in DCM and the reduction/oxidation potentials are much milder than for the SiP\(_{\text{iPr}}\)\(_3\) ligand: −0.3 V (Ru\(^{\text{II}}\)/Ru\(^\text{0}\)) and +0.4 V (Ru\(^{\text{II}}\)/Ru\(^{\text{I}}\)) vs Fc/Fc\(^+\). The
Ru\textsuperscript{I} complex was accessed by one-electron oxidation of the Ru\textsuperscript{II} complex. Interestingly, the ruthenium(\textsuperscript{+I}) complex [Ru\textsuperscript{I}(tropPPh\textsubscript{2})\textsubscript{2}][BF\textsubscript{4}] is only coordinated with two of these bidentate ligands, forming a remarkable 15-electron species with a distorted square planar geometry, as was evidenced by X-ray diffraction analysis. No further reactivity with this complex has been reported to date.

Our group has previously reported the synthesis of the bidentate 3-methylindole-based phosphine phosphoramidite ligands (INDOLPhos).\textsuperscript{[14]} A variation of the INDOLPhos-type ligands is the tetradeinate tris(1-(diphenylphosphanyl)-3-methyl-1H-indol-2-yl) phosphaneligand (1) (Figure 1). This tripodal ligand was simultaneously reported by van der Vlugt \textit{et al.} and Pérez-Prieto \textit{et al.}, and its complexes were prepared with the metals rhodium, iridium, palladium and copper.\textsuperscript{[15–17]} Interestingly, this ligand was shown to stabilize the metallo-radical rhodium complex [Rh\textsuperscript{II}(1)Cl][PF\textsubscript{6}].\textsuperscript{[16]}

Herein we describe our efforts to use the tripodal PP\textsubscript{3}-ligand 1 to stabilize metallo-radical ruthenium(\textsuperscript{+I}) species upon one-electron-reduction of the PP\textsubscript{3}-ligand ruthenium(\textsuperscript{+II}) complex. The above-mentioned previously reported ruthenium(\textsuperscript{+I}) complexes either possess an anionic \(\sigma\)-donating tripodal (SiP\textsubscript{iPr}\textsubscript{3})\textsuperscript{−} ligand or a neutral \(\pi\)-accepting bidentate (tropPPh\textsubscript{2}) ligand. As neutral PP\textsubscript{3}-ligand stabilized examples are thus far unknown, we wondered if such ruthenium(\textsuperscript{+I}) complexes could have a different structure or reactivity. We further wondered if the ruthenium(\textsuperscript{0}) dinitrogen PP\textsubscript{3} complex of ligand 1 was accessible, as we consider such a complex to be of potential interest for N\textsubscript{2} activation. Furthermore, we probed the reactivity of the new, low oxidation state PP\textsubscript{3}-ligand ruthenium(\textsuperscript{+I}) and ruthenium(\textsuperscript{0}) complexes towards dichloromethane and chloroform/styrene mixtures.

### 3.2 Results and Discussion

Ligand 1 was prepared in two steps from 3-methylindole.\textsuperscript{[15,16]} We first investigated the coordination of 1 to ruthenium(\textsuperscript{+II}). The ligand could be coordinated to Ru by reacting stoichiometric amounts of ligand 1 and [RuCl\textsubscript{2} benzene]\textsubscript{2} in refluxing THF to form complex Ru(1)(Cl)\textsubscript{2} (2) (Figure 1) as a yellow powder in almost quantitative yield.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1}
\caption{Coordination of 1 to [RuCl\textsubscript{2}(C\textsubscript{6}H\textsubscript{6})\textsubscript{2}] to form Ru(1)(Cl)\textsubscript{2} (2).}
\end{figure}
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Complex 2 displays three signals in the $^{31}$P-NMR spectrum with an integration of 1:2:1; a doublet of triplets ($\delta$: 100.99 ppm, $J_{P-P}^P = 26.4, 25.5$ Hz), a triplet ($\delta$: 77.76 ppm, $J_{P-P}^P = 26.5$ Hz), and another doublet of triplets ($\delta$: 48.48 ppm, $J_{P-P}^P = 27.9, 26.9$ Hz). This splitting pattern is different than that of the related ruthenium(+II) tripodal tetraphosphine complexes, which were shown to form square pyramidal or trigonal bipyramidal geometries around the metal center.$^{[19,20]}$ In fact, the NMR splitting pattern indicates a different geometry around the metal center. Ruthenium(+II) complexes have preference for 18 valence electron octahedral geometries. An octahedral geometry could explain the observed $^{31}$P-NMR splitting pattern where the two aminophosphine donors in trans position ($\delta$: 77.76 ppm, P1 and P2, Figure 2) are magnetically identical in solution on the NMR time scale and thus appear as one signal with integral 2. The aminophosphine donor P3 trans to the chlorido ligand ($\delta$: 100.99 ppm) is the most deshielded phosphorus atom and the phosphine donor P4 ($\delta$: 48.48 ppm) is the most shielded atom.

Layering of a dichloromethane solution of 2 with pentane resulted in the formation of crystals suitable for single crystal X-ray diffraction. The crystal structure of 2 (Figure 2) indeed shows an octahedral coordination geometry, with an P-Ru-P angle of 160.04(3)$^\circ$ (Table 1) for the two phosphines in trans position (P1 and P2), which is close to the theoretical 180$^\circ$ for octahedral complexes. The Ru-P distance is longest for the bond with the P1-atom (2.3727(9) Å), followed by the P2 atom in trans position (2.3189(9) Å). Similar to other polydentate ruthenium phosphine complexes in literature, the P-donors P3 (2.2671(9) Å) and P4 (2.1932(9) Å) oriented trans to the chlorido ligands have shorter Ru-P distances as compared to the P-donors P1 (2.3727(9) Å) and P2 (2.3189(9) Å) coordinated in mutual trans positions.$^{[21]}$

![Figure 2: ORTEP drawing of 2 (50 % probability ellipsoids). Solvent molecules and hydrogen atoms have been omitted for clarity.](image-url)
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Table 1: Selected bond distances (Å) and angles (°) of the crystal structures of ruthenium complexes with ligand 1 in the oxidation states +II, +I and 0.

<table>
<thead>
<tr>
<th></th>
<th>RuCl(_2)L(_1)(^{II})</th>
<th>RuCl(_2)L(_1)(^{I})</th>
<th>RuN(_2)L(_1)(^{0})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru1–P1</td>
<td>2.3727(9)</td>
<td>2.2930(12)</td>
<td>2.2747(12)</td>
</tr>
<tr>
<td>Ru1–P2</td>
<td>2.3189(9)</td>
<td>2.2940(12)</td>
<td>2.2752(11)</td>
</tr>
<tr>
<td>Ru1–P3</td>
<td>2.2671(9)</td>
<td>2.2717(13)</td>
<td>2.2774(11)</td>
</tr>
<tr>
<td>Ru1–P4</td>
<td>2.1932(9)</td>
<td>2.1956(12)</td>
<td>2.2133(11)</td>
</tr>
<tr>
<td>Ru1–Cl1</td>
<td>2.4869(9)</td>
<td>2.4296(14)</td>
<td></td>
</tr>
<tr>
<td>Ru1–Cl2</td>
<td>2.4471(9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru1–N1</td>
<td></td>
<td>2.011(4)</td>
<td></td>
</tr>
<tr>
<td>N1–N2</td>
<td></td>
<td>1.085(5)</td>
<td></td>
</tr>
<tr>
<td>P1–Ru1–P2</td>
<td>160.04(3)</td>
<td>134.84(5)</td>
<td>122.85(4)</td>
</tr>
<tr>
<td>P1–Ru1–P3</td>
<td>94.27(3)</td>
<td>109.91(4)</td>
<td>118.33(4)</td>
</tr>
<tr>
<td>P2–Ru1–P3</td>
<td>102.23(3)</td>
<td>112.22(5)</td>
<td>115.80(4)</td>
</tr>
<tr>
<td>P1–Ru1–P4</td>
<td>82.67(3)</td>
<td>83.90(4)</td>
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<tr>
<td>P2–Ru1–P4</td>
<td>87.06(3)</td>
<td>84.57(4)</td>
<td>84.14(4)</td>
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<tr>
<td>P3–Ru1–P4</td>
<td>86.85(3)</td>
<td>84.58(4)</td>
<td>84.63(4)</td>
</tr>
</tbody>
</table>

With the aim of exploring the stabilizing effect of ligand 1 for low oxidation states in ruthenium, we attempted to determine the Ru\(^{II}\)/Ru\(^{I}\) and Ru\(^{I}\)/Ru\(^{0}\) reduction potentials of 2. The cyclic voltammogram of 2 in dichloromethane did not show a reduction wave within the window in which the solvent is stable (E\(_{\text{min}}\) = −2.5 vs Fc/Fc'). Unfortunately, the poor solubility of 2 in THF, DMF, acetonitrile and toluene prevented determination of the reduction potentials of 2 below −2.5 V. Thus, if possible at all, the reduction of complex 2 to the desired Ru(1)Cl (3) complex would occur at potentials lower than −2.5 V vs Fc/Fc'. This reduction potential is much lower compared to the reduction potentials needed to form the other ruthenium(+I) complexes as discussed in the introduction, which is a result of the ligand scaffold. As electrochemistry did not show formation of a ruthenium(+I) or ruthenium(0) complex, we investigated if 2 could be reduced chemically. KC\(_8\) was selected as reducing agent, as this reductant is one of the strongest available and has a
reduction potential far lower than $-2.5\, \text{V}$. The addition of one equivalent of KC$_8$ to the yellow suspension of 2 in THF resulted in the formation of a brown NMR-silent solution. This is indicative for the formation of a paramagnetic species formed after one-electron-reduction, which is most likely the metallo-radical species Ru(1)Cl (3) (Figure 3). EPR spectroscopy indeed confirmed formation of the metallo-radical. The X-band EPR spectrum of complex 3 reveals a rhombic, albeit close to axial g-tensor, characteristic for an $S = \frac{1}{2}$ system (Figure 4). Resolved hyperfine couplings (HFIs) with two P-atoms are detected, which is a similar observation as for the (SiP$_3$)$_2$RuI$_2$ complex of the Peters group and other in-situ analyzed tripodal tetradeutate phosphine Ru$^i$ complexes. One phosphorus donor gives rise to large hyperfine couplings, while all HFIs with the other P-donors are much smaller, most of which are not resolved (experimental section: Table 2, and Figure 5). These results are in agreement with a geometry that is in-between a trigonal bipyramidal geometry and a (distorted) square pyramidal coordination geometry around the ruthenium(I) metal center. Preference for such a distorted trigonal bipyramidal coordination geometry, a result of the Jahn-Teller effect, has been observed before for other transition metal complexes with a d$^7$ configuration.

Satisfactory simulations of the experimentally obtained EPR spectra were obtained using the parameters shown in Table 2 (experimental section), as well as in the Figure captions of Figure 4 and Figure 6, and DFT computed EPR parameters (see Table 2) are in qualitative agreement with the experimental data. The computations reveal a mainly
metal-centered spin density distribution, as can be seen from the SOMO and spin density plot of 3 (Figure 5). The SOMO of the metallo-radical complex (spin population at Ru 62%) is essentially the Ru $d_{z^2}$ orbital pointing in the direction of the apical P-donor (P3) of the distorted trigonal bipyramid (Figure 5, left). As a result, the spin population of the axial P-donor (P3) is significant (~12%), thus explaining the observed large HFIIs with this donor atom as mentioned before. The two P-donors in the distorted equatorial plane bind rather asymmetrically, leading to a larger spin population at one of the PPh$_2$ donors (8 %, P2) as compared to the other (5 %, P1). The spin population at the connecting P-donor trans to the chlorido ligand is small and negative (~0.8 %, P4). The resolved HFIIs in the experimental X-band EPR spectrum, stemming from two phosphorus atoms, are thus well explained by the electronic structure of 3. The g-anisotropy of complex 3 is quite small for a metallo-radical complex, but fully understandable considering the large energy separation (Turbomole, BP86, def2-TZVP) between the $d_{z^2}$-dominated SOMO and the filled $d_{xz}$- and $d_{yz}$-dominated MOs (1.4 eV and 1.6 eV, respectively).

The small g-anisotropy of 3 makes it possible to record its EPR spectrum in isotropic solution (Figure 6). A satisfactory simulation of the isotropic spectrum recorded in THF reveals a $g_{\text{iso}}$ value of 2.047 and HFIIs with three equivalent P-atoms ($A_{\text{iso}}^p = 143$ MHz), with the measured $g_{\text{iso}}$ value being close to the average value of the anisotropic g-tensor components ($g_{\text{av}} = (g_x + g_y + g_z)/3 = 2.043$). Detection of HFIIs with three equivalent P-atoms in solution points to rapid positional exchange of the axial and equatorial PPh$_2$ donors on the EPR timescale in the THF solution at room temperature. In agreement, the measured $A_{\text{iso}}^p$ values measured in solution are close to the averaged values of the resolved anisotropic Atensor components stemming from the PPh$_2$ donors measured in frozen solution ($A_{\text{av}}^p = (A_{x}^p + A_{y}^p + A_{z}^p + A_{xz}^p + A_{yz}^p + A_{xy}^p)/9 = 157$ MHz).
Layering of a THF solution of 3 with pentane resulted in the formation of brown needles suitable for single crystal X-ray diffraction analysis. The crystal structure is in good agreement with the EPR data and the DFT calculated structure (Figure 7). The $\tau$-value of 0.70 confirms formation a distorted coordination geometry in between a trigonal bipyramidal and a square pyramidal geometry.\[^{14}\] The P1−Ru−P2 angle is the largest: 134.84(5)°, while the P2−Ru−P3 and P1−Ru−P3 angles are comparable: 112.22(5)° and 109.91(4)° (Table 1).

As one-electron chemical reduction of complex 2 led to the formation of the stable ruthenium(I) complex 3, it seemed promising to also explore the two-electron-reduction of complex 2. Therefore, we decided to add two equivalents of KC₈ to a THF suspension of 2 under N₂ atmosphere in order to reduce the ruthenium(+II) complex, aiming at formation of the ruthenium(0) dinitrogen complex Ru⁰(1)N₂ (4) (Figure 3). After filtration of the reaction mixture, a red solution was obtained, indicating that a reaction had taken place. Subsequent analysis of the filtered solution with infrared spectroscopy showed an absorbance band in the M-N₂ area. The peak found in the infrared spectrum at $\nu_{N_2} = 2125$ cm⁻¹ represents a weakly activated dinitrogen bond as a result of slight $\pi$-back-donation of the ruthenium metal to the diatomic ligand. The $^{31}$P-NMR spectrum of the solution showed two peaks in a 3 : 1 ratio: a doublet and a quartet with a coupling constant...
of $J^{P-P} = 39$ Hz. This coupling is in agreement with a $C_3$-symmetrical complex where the three peripheral phosphine atoms are equivalent and couple with the central P-atom at the axial position.

Brick red crystals suitable for X-ray diffraction were grown by diffusion of pentane vapor into a THF solution of the filtered reaction mixture. The molecular structure, determined by X-ray diffraction, indeed proves formation of the dinitrogen complex 4.
(Figure 8). Complex 4 has a trigonal bipyramidal geometry ($\tau_5 = 0.93$)\textsuperscript{[24]}, as is expected for a 5-coordinate 18 valence electron species (Table 1). The three peripheral P–Ru–P angles are similar, all being close to 120°, thus, P1 and P2 are not in trans position anymore (see further). The P1–P2–P3 plane slightly bends down towards P4 (all around P$_{eq}$–Ru–P4 angles are around 84°) and the P4–Ru distance is larger (2.2133(11) Å) than found for complexes 2 and 3 as a result of the dinitrogen ligand in trans position, which is competing for the same n-back donating orbital of the metal. The P3–Ru distance is on average the same in all three oxidation states. However, comparison of the bond distances of the trans phosphines (P1–Ru and P2–Ru) for complexes 2, 3 and 4 reveals an unexpected behavior. Going from an electron-poor to an electron-rich metal center (from 2 to 3 to 4) the P1–Ru and P2–Ru bond distances become shorter. This trend is likely an interplay of several effects, the first being steric. Going from an octahedral 6-coordinate species (Ru$^{II}$) to a trigonal bipyramidal 5-coordinate species (Ru$^{I}$), less steric hindrance between the atoms plays a role for the Ru$^{I}$ complex, resulting in the shortening of the Ru–P bond distances. The Ru$^{I}$ complex still has a very distorted trigonal bipyramidal geometry around the metal center ($\tau_5 = 0.70$)\textsuperscript{[24]}, as a result of the Jahn-Teller distortion. This metallo-radical complex causes a more strained complex, and hence longer Ru–P bond distances compared to the trigonal bipyramidal geometry of the Ru$^{0}$ ($\tau_5 = 0.93$)\textsuperscript{[24]}, which minimizes the steric repulsion between the ligands in the ‘trigonal plane’ and therefore complex 4 has the shortest bond distances. Another factor that can play a role is that these two phosphorus atoms compete for the same electrons of the metal the more trans they are positioned: the most trans (Ru$^{II}$) thus leads to the longest bond, and Ru$^{0}$, which has a P1–Ru–P2 angle of 122.85(4)°, thus leads to the shortest bond. A third factor is that these amino phosphines (P1, P2 and P3) are n-acidic, which makes that the highest electron density (Ru$^{0}$) strengthens, thus shortens these P–Ru bonds as a result of stronger n-back-donation of the metal into the antibonding orbitals of the amino phosphines.

As two-electron-reduction of complex 2 showed coordination of dinitrogen to the ruthenium(0) center forming complex 4, we subsequently explored catalytic dinitrogen reduction with 2. Complex 2 was reacted with KC$_8$ (50 equiv.) and [H(OEt)$_2$]$_2$[BArF$_4$] (50 equiv.) at −78 °C in THF and stirred under dinitrogen atmosphere overnight (Figure 9). Unfortunately, no traces of ammonia were detected in the reaction mixture.

\[
\begin{align*}
2 & \\
KC_8 & (50 \text{ equiv.}) \\
[H(OEt)_2][BArF_4] & (50 \text{ equiv}) \\
N_2 & \xrightarrow{x} \text{NH}_3 \\
-78 \degree \text{C, 16 h} & 
\end{align*}
\]

**Figure 9:** Dinitrogen reduction to ammonia with complex 2.
Next, we explored the reactivity of the low oxidation state ruthenium complexes with alkyl chlorides. Roper, and later also the group of Grubbs, reported the formation of dichlorido ruthenium(+II) carbenes upon addition of α,α-dihalido and trihalido compounds to Ru\(^0\) complexes, where both the chlorides and the carbene originate from the organohalide (Figure 10).\(^{[25,26]}\) The reaction is proposed to proceed through oxidative addition of the Cl–C bond, followed by α-chlorido elimination of the Cl–R yielding the dichlorido ruthenium carbene.

A copper complex that was prepared with ligand 1 was previously shown to dissociate one of the phosphine arms dissociated from the metal center.\(^{[16]}\) Such a dissociation could facilitate the formation of the dichlorido ruthenium carbene complex, as this will lead to the formation of a preferred 6-coordinate ruthenium(+II) complex, rather than the unfavorable 7-coordinate species upon the reaction of α,α-dihalido and trihalido compounds with Ru\(^0\) complex 4. Thus, we set out to explore the reactivity of 4 with dichloromethane. Surprisingly, dissolution of complex 4 in dichloromethane resulted in the formation of the oxidized ruthenium(+II) complex 2, as was evidenced by in situ \(^{31}P\)-NMR spectroscopy (see experimental section). As no other ruthenium complexes were detected in the \(^{31}P\)-NMR spectrum, a different type of reaction has taken place. A possible reaction that could take place is a radical mechanism in which two radicals are stepwise abstracted from an organohalide by the ruthenium complex, causing a one-electron oxidation of the metal center per radical abstraction. This means that the reaction of Ru\(^0\) complex 4 with dichloromethane to form Ru\(^{II}\) complex 2 proceeds through Ru\(^{I}\) complex 3. To test this hypothesis, we added two drops of dichloromethane to a suspension of 3 in THF-d\(_8\) in a high-pressure NMR-tube. This brown suspension turned gradually to a light brown-colored solution within three days and the \(^{31}P\)-NMR spectrum that was measured

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**Figure 10:** Left: reactivity in literature of ruthenium complexes with Cl–C bonds. Right: the in this work experimentally investigated reactions of our ruthenium complexes with dichloromethane and chloroform.
after 1 and 3 days showed formation of the ruthenium(+II) complex \(2\) in time. In addition, no signals corresponding to Ru\(^{\text{I}}\) complex \(3\) were found when the reaction mixture was measured with EPR-spectroscopy, which indeed shows that complex \(3\) can be oxidized by one-electron with dichloromethane. Complex \(2\) is stable in dichloromethane or chloroform and does not react further to the Ru\(^{\text{III}}\) adduct, which is likely a result of the rigid tetradentate ligand, that keeps the ruthenium(+II) complex from reacting further. Radical abstraction from \(\alpha,\alpha\)-dihalido and trihalido compounds is a known reaction for Ru\(^{\text{II}}\) complexes, as it is also a key step in the Kharasch reaction or the nowadays more commonly called atom transfer radical addition.\(^{27,28}\) In this addition reaction an organohalide is added to a vinyl group, which is catalyzed by a Ru\(^{\text{II}}\) complex (Figure 10). The reaction is initiated by the Cl\(^{\cdot}\) radical abstraction of the organohalide by the Ru\(^{\text{II}}\) complex forming the one-electron oxidized Ru\(^{\text{III}}\)Cl complex. The remaining R\(^{\cdot}\) fragment adds to the double bond, followed by radical-radical recombination, and reduction to form the Ru\(^{\text{II}}\) complex. We decided to investigate whether a similar mechanism could also be possible with complexes \(3\) and \(4\) as they were able to abstract chloride radicals from dichloromethane, leading to the oxidized complex \(2\). We anticipated that the last step of the Kharasch reaction would be the hardest with our complexes, as this involves reduction of the ruthenium complex. The reduction potentials of complex \(2\) lie below \(-2.5\) V vs Fc/Fc\(^{\text{+}}\), thus requiring very strong reducing agents. Therefore, we decided to explore the reactivity of complex \(3\) (which is easier to reduce) in the addition reaction of chloroform to styrene. The reaction of \(3\) with chloroform and styrene in THF-d\(_8\) at 60 \(^\circ\)C was followed in time. Unfortunately, no new peaks corresponding to the Kharasch addition product were observed in \(^1\)H-NMR spectroscopy. However, the chloroform peak did slightly decrease in time accompanied by the formation of a yellow precipitate. Analysis of this yellow precipitate by \(^{31}\)P-NMR spectroscopy indicated the presence of the oxidized ruthenium(II) \(2\) complex. These results show that complex \(3\) is able to abstract a chloride radical under Kharasch conditions, but does not donate the chloride radical back. Likely, complex \(2\) is too stable and does not get reduced back to complex \(3\) under these conditions. This is in line with the CV experiments of complex \(2\) in dichloromethane, which did not show a reduction wave until \(-2.5\) V vs Fc/Fc\(^{\text{+}}\).

### 3.3 Conclusions

In conclusion, we have shown the formation of a new ruthenium(+II) complex based on a tripodal tetrathiolphosphine indolyl ligand. The complex can be reduced forming a rare ruthenium(+I) and a ruthenium(0) dinitrogen complex, thereby showing that the scaffold can stabilize low oxidation states of ruthenium. The three oxidation states of
ruthenium with the indolyl ligand are identified with NMR or EPR spectroscopy, and were further confirmed by X-ray diffraction analysis. The ruthenium(II) complex was evaluated for catalytic dinitrogen reduction to ammonia, but unfortunately no product could be detected in the reaction mixture. However, the Ru⁺ and Ru⁰ complexes are shown to abstract a Cl⁻ radical from either dichloromethane or chloroform leading back to the stable parent Ruᴵᴵ⁺ complex, which appears to be the most stable form of ruthenium in this ligand framework. So far, these are stoichiometric reactions. Further tuning of the complex (ligand modification, type of metal) is required to turn this into catalytic analogues.

3.4 Experimental Section

General methods
All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques or in the glovebox. Reagents were purchased from commercial suppliers and used without further purification. THF, pentane, hexane and Et₂O were distilled from sodium benzophenone ketyl, CH₂Cl₂ was distilled from CaH₂ under nitrogen. NMR spectra (¹H, ³¹P, and ¹³C{¹H, 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. Ligand 1 was prepared in two steps from 3-methylindole.¹⁵,¹⁶ KC₈ was prepared by the method of Rabinovitz¹⁷ which yielded a finely dispersed brown powder.

EPR spectroscopy
Experimental X-band EPR spectra were recorded on a Bruker EMX spectrometer equipped with a He temperature control cryostat system (Oxford Instruments). The spectra were simulated by iteration of the anisotropic g-values, (super)hyperfine coupling constants and line widths using the W95EPR program (available upon request from Prof. Frank Neese, University of Bonn).

DFT and EPR property calculations
The geometry of the full atom model of 3 was fully optimized with the Turbomole program¹⁸ coupled to the PQS Baker optimizer¹⁹ at the BP86 level²⁰ using the def2-TZVP basis,²¹ with and without Grimme’s version 3 dispersion corrections (DFT-D3, disp3, zero damping²²). EPR parameters²³ were subsequently calculated with both the ADF²⁴ and Orca²⁵ program systems, using the coordinates from the structure optimized in Turbomole as input. In the ADF calculations we used the (Gaussian-defined) B3LYP
functional with the ZORA/TZ2P basis set supplied with the program (all electron, core double zeta, valence triple zeta polarized basis set on all atoms), and the unrestricted COLLINEAR approach. In the Orca calculations we used the Ahlrich’s def2-TZVP basis set and the (Turbomole-defined) b3lyp functional.

**Synthesis of compounds**

**Complex 2:** 1 (348.5 mg, 0.36 mmol) and \([\text{RuCl}_2(\text{C}_6\text{H}_6)_2]\)_2 (89.6 mg, 0.18 mmol) were suspended in THF (6 mL) and stirred at 60 °C overnight. After cooling the yellow precipitated complex was filtered off, washed with THF (3 x 2 mL) and pentane (3 x 3 mL) and dried overnight in the vacuum oven at 40 °C. Recrystallization of the complex by layering a DCM solution with pentane at 5 °C gave crystals suitable for X-ray diffraction analysis. Yield: 0.3968 g of a yellow solid (97%).

- **^1H**-NMR (300 MHz, CDCl₃): δ 7.66 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.51 – 7.40 (m, 4H), 7.22 – 7.08 (m, 10H), 7.06 (d, J = 7.5 Hz, 1H), 7.01 – 6.89 (m, 8H), 6.84 (td, J = 7.5, 5.3 Hz, 4H), 6.77 – 6.61 (m, 5H), 6.56 (t, J = 7.3, 1.4 Hz, 4H), 6.20 (d, J = 8.4 Hz, 2H), 5.82 (d, J = 8.5 Hz, 1H), 2.87 (s, 6H), 2.63 (s, 3H) ppm.

- **^31P**-NMR (162 MHz, CDCl₃): δ 104.80 (dt, J = 28.0, 27.1 Hz, 1P), 81.63 (t, J = 26.3 Hz, 1P), 52.36 (dt, J = 28.2 Hz, 1P) ppm.

- **^13C{^1H,^31P}**-NMR (75 MHz, CDCl₃): δ 139.99, 139.89, 139.44, 139.34, 136.46, 136.38, 135.49, 135.42, 134.80, 134.45, 134.01, 132.99, 132.85, 132.71, 132.61, 131.91, 131.82, 131.48, 131.43, 131.37, 131.28, 129.65, 129.44, 129.27, 128.16, 128.13, 127.69, 127.61, 126.32, 126.27, 123.98, 123.84, 121.74, 121.59, 120.45, 120.38, 117.27, 117.23, 12.13 (CH₃), 11.92 (CH₃) ppm. 

**Mass analysis** (CSI) \([\text{2-Cl}]^+\): found: 1110.1824, calc: 1110.1779; \([\text{2-Cl-HCl}]^+\) found: 1074.2038, calc: 1074.2095.

**Complex 3:** 2 (103.8 mg, 0.09 mmol) and KC₈ (Strem, 15.9 mg, 0.12 mmol) was transferred to a Schlenk flask in the glovebox, stirred in 10 mL THF and stirred for two days leaving a brown solution with yellow solids. The solution was filtered off, evaporated to dryness and extracted with 3 x 1 mL of THF. Pentane was added to this THF solution, until all 3 had precipitated. The brown solid was collected and dried. Yield: 14.4 mg (14 %). Alternatively, the THF solution of 3 was layered with pentane, resulting in the formation of crystals suitable for X-ray diffraction. The EPR spectrum was measured in THF, for the frozen measurement \([\text{Bu}_4\text{N}]\)(PF₆) was added. **Mass analysis** (CSI) \([\text{3-Cl}]^+\): found: 1075.2038, calc: 1075.2095.
Complex 4: 2 (94.0 mg, 0.082 mmol) and KC₈ (homemade, 25.6 mg, 0.19 mmol) were transferred to a Schlenk flask in the glovebox, suspended in 1.7 mL of THF and stirred for 2 hours. The red solution with black solids was filtered and set for crystallization by diffusion of pentane vapor into a THF solution of 4 yielding single crystals suitable for x-ray diffraction analysis. Yield: 33.7 mg (37 %).

1H-NMR (300 MHz, THF-‐d₈): δ 7.48 (d, J = 8.0 Hz, 3H), 7.03 (t, J = 7.0 Hz, 3H), 6.88 (d, J = 8.3 Hz, 30H), 6.67 (t, J = 7.8 Hz, 3H), 6.40 (d, J = 8.4 Hz, 3H), 2.54 (s, 9H) ppm. 31P-NMR (122 MHz, THF-‐d₈): δ 97.93 (d, J = 39.0 Hz, 3P), 52.22 (q, J = 39.2 Hz, 1P) ppm. 13C{1H, 31P}-NMR (75 MHz, THF): δ 129.33 (s, CH-ph), 127.82 (m, CH-ph), 127.07 (m, CH-ph), 122.83 (s, CH-ind), 119.95 (s, CH-ind), 119.67 (s, CH-ind), 115.21 (s, CH-ind), 9.49 (s, CH₃) ppm. (quaternary carbon peaks were not resolved) νₙ₂ = 2025 cm⁻¹. Mass analysis (CSI) [4-H]: found: 1074.2006, calc: 1074.2016.

Alternative method for the synthesis of complex 4: 2 (165.3 mg, 0.145 mmol) and 10% Na/Hg (67.9 mg, 0.30 mmol) were transferred to a Schlenk flask equiped with a glass stirring bean in the glovebox, suspended in 10 mL THF and stirred for 2 days. The red solution with mercury particles was evaporated to dryness, extracted with benzene (2, 1 and 1 mL) and dried in vacuo. Yield: 168.8 mg (83 %).

Reaction of 2 with KC₈ and [H(OEt₂)₂][BARF₄]
2 (35.3 mg, 0.031 mmol) and KC₈ (218.9 mg, 0.69 mmol) were transferred to a Schlenk flask in the glovebox. THF (7 mL) was added and the suspension was stirred for 2 minutes after which the solution was frozen. To this frozen solution the [H(OEt₂)₂][BARF₄] (1.6003 g, 0.69 mmol) dissolved in THF (3 mL) was added, after which the suspension was warmed to −78 °C and stirred overnight. The amount of ammonia present the reaction mixture was quantified via the indophenol method.[39]

Reaction of 4 with dichloromethane
2 (166.3 mg, 0.145 mmol) and Na/Hg (33.2 mg, 0.14 mmol) were stirred in 10 mL of THF in the glovebox for 4 days. A red-brown solution with unreacted yellow solids of 2 formed. In situ 31P-NMR analysis of the filtrate (± 0.35 mL) showed the presence of 4. 1 drop of CH₂Cl₂ was added to this NMR tube and left for 1 day. In situ 31P-NMR analysis of this lighter brown solution the next day showed full conversion to 2.

Reaction of 3 with dichloromethane
3 (4.5 mg, 4.0 μmol) was dissolved in 0.3 mL of THF-d₈. After conformation of the absence of 2 in this brown solution by 31P-NMR spectroscopy, 2 drops of dichloromethane were added. This addition caused a gradual color change (2 days) to light brown and in situ 31P-NMR analysis showed formation of 2.
Chapter 3

Reaction of 3 with chloroform and styrene

3 (9.9 mg, 8.9 μmol) was heated together with styrene (1 equiv.) and chloroform (1 equiv.) dissolved in 0.3 mL of THF-d₈ at 60 °C. After two hours, a yellow precipitate formed. Analysis of this yellow precipitate confirmed formation of 2. No new products corresponding to the Kharasch reaction were detected in ‘H-NMR.

EPR measurement of 3

Table 2: Experimental and DFT calculated EPR parameters of 3.

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<th>DFT (c)</th>
<th>DFT (b)</th>
<th>DFT (b)</th>
<th>DFT (c)</th>
<th>DFT (c)</th>
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a) Parameters from spectral simulations (least square ‘best fit’).

Hyperfine couplings and line width parameters in MHz. NR = not resolved.

b) DFT calculated EPR parameters (Orca, b3-lyp, def2-TZVP).

c) DFT calculated EPR parameters (ADF, B3LYP, TZ2P).

d) Optimized with Turbomole (BP86, def2-TZVP).

e) Optimized with Turbomole (DFT-D3 (disp3), BP86, def2-TZVP).
**Single crystal X-ray diffraction**

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. Multiscan absorption correction and scaling was performed with SADABS. The structure was solved with Intrinsic Phasing Methods using SHELXT. Least-squares refinement was performed with SHELXL 2013 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. RuCl$_2$L$_1$H had 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.

### Table 3: Crystallographic data for RuCl$_2$L$_1$H, RuClL$_1$H and RuN$_2$L$_1$H.

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<th>RuClL$_1$H</th>
<th>RuN$_2$L$_1$H</th>
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<td><strong>Empirical formula</strong></td>
<td>$C_{63}H_{51}ClN_3P_4Ru$, 3(CH$_2$Cl)$_2$ + solvent</td>
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<td>$C_{63}H_{51}ClN_3P_4Ru$, $C_4H_8O$</td>
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$^a$ Excluding the disordered solvent contribution.
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References


[31] (a) PQS version 2.4, 2001, Parallel Quantum Solutions, Fayetteville, Arkansas, USA (the Baker optimizer is available separately from PQS upon request); (b) J. Baker *J. Comput. Chem.* 1986, 7, 385.


[33] (a) Turbomole basis set library, Turbomole Version 5, see [30]; (b) A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* 1994, 100, 5829.


Chapter 3


[41] Sheldrick, G. M. SADABS and TWINABS - Universität Göttingen, Germany; 2008.

