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

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Chapter 5

Coordination of 3-methylindole-based tripodal tetraphosphine ligands to iron(II), cobalt(II) and nickel(II) and investigations of their subsequent two-electron-reduction
Chapter 5

5.1 Introduction

In Chapters 3 and 4 of this thesis, the coordination of tripodal indolyl-based tetraphosphine ligands to ruthenium have been discussed. The obtained ruthenium(+II) complexes revealed interesting redox chemistry. One-electron-reduction led to a rare paramagnetic ruthenium(+I) complex, while two-electron-reduction allowed for the formation of dinitrogen complexes. Moreover, modifications of the electronic properties of the ligand showed a significant effect in the dinitrogen bond activation and in the catalytic performance of the complexes in formic acid dehydrogenation. These intriguing results triggered us to further explore the coordination behavior of the tripodal indolyl-based ligands with other transition metals. In particular, expanding the coordination chemistry of these tetradentate ligands to base metals seemed to be most compelling, as complexes of tripodal phosphine ligands with base metal iron and cobalt reveal outstanding activity in for example dehydrogenation/hydrogenation of C-based fuels or reduction of N₂.[1–4]

The use of first row transition metal complexes rather than second or third row transition metals is also key to a more sustainable future, as first row transition metals are earth abundant, benign, non-toxic and inexpensive.[5–7]

Thus, we set out to first explore the coordination chemistry of the tripodal indolyl-based tetraphosphine ligands (PP₃) to the earth abundant iron, cobalt and nickel. Tripodal tetradeutate phosphine based complexes using either PP₃ph = P(CH₂CH₂PPh₂)₃ or PP₃iPr = (P(CH₂CH₂P)iPr₂)₃ coordinated to iron(+II), cobalt(+II) and nickel(+II) have been extensively studied in literature.[8–13] These tripodal ligands generally occupy four coordination sites around a metal center and a trigonal bipyramidal geometry (TBP) is the most commonly observed geometry when the ligand is coordinated to a first row transition metal center.[12,14] These [MX(PP₃)]⁺ complexes are formed by reacting the corresponding MX₂ salt with the ligand in the presence of a non-coordinating anion and can subsequently be reduced leading to the coordination of dinitrogen to the metal center. Tripodal tetradentate phosphine metal complexes where dinitrogen is bound to the metal center, have been isolated for both cobalt and iron: [CoIIN₂(PP₃Ph)⁺ (νN₂ = 2125 cm⁻¹)]¹⁵ and Fe₀N₂(PP₃iPr) (νN₂ = 1985 cm⁻¹).[16] Nickel dinitrogen complexes are scarce:[17] only one example with a tripodal ligand exists, which is a complex based on the anionic tridentate phosphine ligand [SiP₃iPr–SiP₃iPr–]⁻ (SiP₃iPr = tris[2-(diisopropylphosphino)-phenyl]silane) ligand, leading to a weakly activated dinitrogen bond (νN₂ = 2223 cm⁻¹) in the [NiII(N₂(SiP₃iPr))][BarF₄] complex.[18] Also the iron(+I) and cobalt(+I) dinitrogen complexes with this [SiP₃iPr–]⁻ ligand were prepared, showing much stronger activation of the dinitrogen bond as a result of the higher energy of the d-orbitals of the metals, which decreases by going from left to right of the row in the periodic table (see Chapter 1): Fe⁺N₂(SiP₃iPr)⁻ (νN₂ =
2003 cm\(^{-1}\)) and \(\text{Co}^2\text{N}_2(\text{SiP}^\text{Pr}_3)\) (\(\nu_{\text{N}_2} = 2063\) cm\(^{-1}\))\(^{[19,20]}\) As mentioned before, since tripodal complexes generally occupy four coordination sites of the complex, the corresponding cobalt(+I) and nickel(+II) dinitrogen complexes would lead to the formation of a favorable 18-electron complex.

This chapter is organized in two sections. In the first section the coordination of tripodal indolyl-based tetraphosphine ligands to the first-row late transition metals iron, cobalt, and nickel is explored. First the coordination of ligand \(\text{L}^\text{I}^\text{H}\) to these metals is investigated. Single crystal X-ray structure determination of these complexes allowed to study the changes in the coordination geometry of the ligand while stepwise increasing the d-electron count from \(d^6\) to \(d^7\) to \(d^8\) by going from iron(+II) to cobalt(+II) to nickel(+II). Additionally, coordination studies of a variety of 3-methylindole based ligands (\(\text{L}^\text{I}^\text{H}, \text{L}^\text{H}^\text{H}\) and \(\text{L}^\text{I}^\text{Pr}\)) to iron(+II) and the synthetic challenges involved during coordination of these ligands to iron are reported.

In the second section the electrochemical and chemical reduction of the above-mentioned complexes is explored. Electrochemical reduction is used to evaluate if these complexes are redox-active. We further investigate whether two-electron-reduction with \(\text{KC}_8\) in the presence of dinitrogen would lead to coordination of the \(\text{N}_2\) ligand to the various metal complexes, as coordination of dinitrogen is a prerequisite for dinitrogen reduction to ammonia. For the cobalt and nickel complexes the coordination of dinitrogen would likely require the dissociation of one of the ligand arms, to form a favorable 18-electron complex. In addition, we explored whether ligand modification leads to observable electronic effects in the \(\text{N}=\text{N}\) stretch frequency when the \(\text{PP}_3\) ligand is coordinated to iron. Additionally, the changes in the coordination geometry of the iron complexes upon reduction are discussed based on the crystal structures of iron(+I) complexes with ligands \(\text{L}^\text{I}^\text{H}, \text{L}^\text{H}^\text{H}\) and \(\text{L}^\text{I}^\text{Pr}\) and iron(0) with ligand \(\text{L}^\text{I}^\text{H}\).

5.2 Results and discussion

Section 1: Coordination studies of \(\text{PP}_3\) ligands to iron, cobalt and nickel and.

Formation of mono and binary cobalt \(\text{L}^\text{I}^\text{H}\) complexes

We initially explored the coordination of the tripodal indolyl-based tetraphosphine ligand (\(\text{L}^\text{I}^\text{H}\)) to cobalt(+II). The formation of the \([\text{CoL}^\text{I}^\text{H}][\text{BF}_4]\) complex was performed by the addition of stoichiometric amounts of \(\text{L}^\text{I}^\text{H}\) to the \(\text{CoCl}_2\) salt in THF in presence of \(\text{NaBF}_4\) (Figure 1). It was anticipated that in the absence of \(\text{NaBF}_4\) a tetrachlorido cobaltate(+II) dianion (see refs: \([21-28]\)) would form. Therefore, we reacted \(\text{L}^\text{I}^\text{H}\) with \(\text{CoCl}_2\) in a 2 : 3
stoichiometry to form the binary $[\text{CoCl}\text{L1}^\text{H}]_2[\text{CoCl}_4]$ complex. After stirring the brown suspensions overnight, analysis of the filtrates indicated full conversion as no signals of free ligand were detected by $^{31}\text{P}-\text{NMR}$ spectroscopy.

Cold Spray Ionization (CSI) mass spectroscopy analysis showed the presence of the $[\text{CoCl}\text{L1}^\text{H}]^+$ ion in both $[\text{CoL1}^\text{H}][\text{BF}_4]$ and $[\text{CoCl}\text{L1}^\text{H}][\text{CoCl}_4]$ samples (see experimental section). Similar to findings reported by Braunstein et al. the $[\text{CoCl}\text{L1}^\text{H}]_2[\text{CoCl}_3]^+$ fragment could be detected in the $[\text{CoCl}\text{L1}^\text{H}][\text{CoCl}_4]$ sample, indicating formation of the proposed binary complex. Both the cationic and anionic cobalt complexes are paramagnetic. EPR analysis of the $[\text{CoL1}^\text{H}][\text{BF}_4]$ and $[\text{CoCl}\text{L1}^\text{H}][\text{CoCl}_4]$ complexes in THF at 20 K are indicative for an $S = \frac{1}{2}$ system with the cobalt(II) ion being in a low spin configuration (Figure 2). Small hyperfine couplings with cobalt and the phosphine atoms are also noticeable. In addition, $[\text{CoCl}\text{L1}^\text{H}][\text{CoCl}_4]$ shows an extra signal (700-2500 G) corresponding to the high spin tetrachlorido cobaltate anion, which is absent in the $[\text{CoL1}^\text{H}][\text{BF}_4]$ complex.

Layering a dichloromethane solution of $[\text{CoCl}\text{L1}^\text{H}][\text{CoCl}_4]$ with pentane resulted in the formation of crystals suitable for X-ray diffraction analysis (Figure 3). As expected the binary complex $[\text{CoCl}\text{L1}^\text{H}][\text{CoCl}_4]$ is present in the crystal structure. The two $[\text{CoCl}\text{L1}^\text{H}]^+$ units crystallize as two independent molecules, which possess a very distorted geometry around the metal center, almost in-between a trigonal bipyramidal and square pyramidal geometry ($\tau_{5/3} = 0.55$ and $\tau_{5/3} = 0.67$) (Table 1). This distortion is a result of the Jahn-Teller effect in combination with the rigidity of the backbone, which was also observed for the rhodium(II) $[\text{RhCl}\text{L1}^\text{H}][\text{PF}_6]$ complex ($\tau = 0.55$). The four strong-field phosphine
ligands favor the formation of low spin complexes, thus, d\(^7\) complexes tend to form square pyramidal geometries. However, the rigidity of the ligand scaffold limits the structural movement, resulting in a geometry in-between trigonal bipyramid and a square pyramid. This is different for the iron and the nickel analogues (vide infra) as these complexes possess intermediate spin d\(^6\) or low spin d\(^8\) metals, respectively and thus have a preference for the TBP geometry with this ligand scaffold.

**Figure 2:** EPR spectrum of \([\text{CoL1H}]\text{[BF}_4]\) and \([\text{CoClL1H}][\text{CoCl}_4]\).

**Figure 3:** ORTEP drawing of \([\text{CoClL1H}][\text{CoCl}_4]\) (50% probability ellipsoids). Hydrogen atoms, solvent molecules and phenyl rings on the phosphor atoms have been omitted for clarity.
Table 1: Selected bond distances of the [M\(^{II}\)L\(^+\)] complexes.

<table>
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<td>137.07(4)</td>
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<td>Cl1–M1–P4</td>
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Table 1-continued: Selected bond distances of the [M\(^{II}\)L\(^+\)] complexes.

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<td>2.1952(8)</td>
<td>2.1729(11)</td>
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<tr>
<td>M1–Cl1</td>
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<td>P1–M1–P2</td>
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<td>Cl1–M1–P4</td>
<td>178.58(4)</td>
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Formation of mono and binary nickel L1\(^{+}\) complexes

Similar to the cobalt complex, the coordination of nickel to L1\(^{+}\) resulted in the formation of either the [NiL1\(^{+}\)][BF\(_4\)] or the [NiClL1\(^{+}\)]\(_2\)[NiCl\(_4\)] complexes, depending on the use of NaBF\(_4\) during the synthesis (Figure 4). As expected for the pentacoordinate d\(^8\) complexes with strong-field phosphorus ligands, the [NiL1\(^{+}\)]\(^+\) cations are diamagnetic, and thus NMR analysis of the complexes was possible. The identical \(^{31}\)P-NMR spectra of NiL1\(^{+}\)BF\(_4\) and [NiClL1\(^{+}\)]\(_2\)[NiCl\(_4\)] show one doublet (61.06 ppm) and one quartet (25.91 ppm), indicating a C\(_3\)-symmetrical trigonal bipyramidal geometry in solution on the NMR time scale.

Symmetrical diamagnetic complexes of tripodal tetradentate phosphines coordinated to nickel have been previously reported\(^{12,32}\) and trigonal bipyramidal geometry was also reported for the d\(^8\) RuN\(_2\)L1\(^{+}\) (Chapter 3) and the [PdClL1\(^{+}\)]\(_2\)[Cl]\(_3\) complexes. Interestingly, whereas the coordination of nickel to L1\(^{+}\) results in the formation of the binary [NiClL1\(^{+}\)]\(_2\)[NiCl\(_4\)] complex, the palladium complex does not form the tetrachlorido palladate, but one of the chloride anions remains non-coordinating. In accordance with the NMR data, CSI mass spectrometry analysis showed the presence of the [NiClL1\(^{+}\)]\(^+\) ion in both NiL1\(^{+}\)BF\(_4\) and [NiClL1\(^{+}\)]\(_2\)[NiCl\(_4\)] (see experimental section). Slow diffusion of hexane vapors to a dichloromethane solution of [NiClL1\(^{+}\)]\(_2\)[NiCl\(_4\)] resulted in the formation of crystals suitable for X-ray diffraction analysis (Figure 5).

The crystal structure shows the presence of the binary [NiClL1\(^{+}\)]\(_2\)[NiCl\(_4\)] complex where the two [NiClL1\(^{+}\)]\(^+\) units crystallize as two independent molecules. The [NiClL1\(^{+}\)]\(^+\) units feature a distorted trigonal bipyramidal geometry around the metal center (\(\tau_{5\pi} = 0.70\) and...
The geometry is less distorted than the cobalt analogues (vide supra), but more distorted than the iron analogue, which is likely a result of the smaller atomic radius of the nickel atom compared to iron (vide infra). The largest angle P1–Ni–P2 is 131.39(4) ° for one structure and 126.51(4) ° for the other, which is still close to the ideal 120 ° angle for the TBP geometry.

Formation of iron PP$_3$ complexes

The above results show that the coordination of the tetradeutate indolyl phosphate ligand L$_1$H to d$^8$ nickel(+II) and d$^7$ cobalt(+II) chlorides results in formation of (distorted in the case of cobalt) trigonal bipyramidal complexes of the type [M$^{II}$ClL$_1$H]$^+$ and that in the absence of non-coordinating BF$_4^-$ anion, binary tetrachlorido metallate complexes are formed. In the following section, we turn our attention to iron. Whereas in the case of nickel and cobalt these complexes are pentacoordinate, complexation of d$^6$ iron(+II) with the L$_1$H ligand could in principle either result in formation of a hexacoordinate 18 VE complex, as was observed for iron’s heavier analog ruthenium (see Chapters 3 and 4), or in formation of a pentacoordinate 16 VE complex. Thus, we decided to study the coordination chemistry of iron in more detail, including the use of other tripodal indolyl phosphate ligands. The reaction of FeCl$_2$ with L$_1$H and NaBF$_4$ in THF in a 1:1:1 stoichiometry led to full conversion of the ligand according to the absence of its $^{31}$P-NMR signal, and the formation of a purple, paramagnetic complex as judged by the presence of broad peaks in the $^1$H-NMR spectrum in the region of 16.24 to 9.14 ppm. The paramagnetic behavior
hinted at the formation of a 5-coordinate species, rather than the octahedral 6-coordinate geometry found for the RuCl$_2$ L complexes (see Chapters 3 and 4). CSI mass spectrometry analysis shows the presence of both the [FeClL$_1$H]$^+$ and the [BF$_4^{-}$] fragment, which is in accordance with a five-coordinate geometry around the metal center, supported by one non-coordinating anion. These data thus indicate that the synthesized compound is a pentacordinate iron complex [FeClL$_1$H][BF$_4$]. DFT calculations suggest that the lowest energy state of the [FeClL$_1$H]$^+$ cation is an intermediate spin, paramagnetic trigonal bipyramidal complex.$^{[34]}$ Many iron(+II) (d$^6$) complexes coordinated to bulky tripodal phosphine ligands possess the TBP geometry, which can indeed result in paramagnetic complexes.$^{[11,13,16,35,36]}$ Crystals suitable for X-ray diffraction were obtained by layering a dichloromethane solution of [FeClL$_1$H][BF$_4$] with pentane.

Figure 6: Synthesis of L$_3^{iPr}$ and coordination of L$_1^{CF_3}$, L$_1^{OMe}$, L$_3^{iPr}$ and L$_2^{H}$ to FeCl$_2$ in the presence of NaBF$_4$. 

tris-2-(3-methylindolyl)phosphine
As anticipated, the crystal structure shows a trigonal bipyramidal geometry around the metal center (Figure 7). The overall crystal structural data is in good agreement with other tripodal 5-coordinate tetraphosphine TBP iron(+II) complexes.\cite{4,11,16,36,37} The longest equatorial angle P1–Fe1–P2 of 120.51(4)° fits well with that of an ideal TBP geometry, which is in correspondence with a $\tau_5 = 0.92$\cite{30}.

It is interesting to compare the coordination chemistry of $L_1^H$ to iron(+II) with that to ruthenium(+II). In the complex of iron(+II)chloride with $L_1^H$ the pentacoordinate geometry with one of the chlorido ligands dissociated is preferred while for ruthenium(+II) chloride hexacoordinate geometry with both chlorido ligands coordinated was observed (see chapter 3). The most likely reason for that is the smaller atomic radius of iron as compared to ruthenium, which results in shorter ligand to metal distances for iron. This results in steric crowding around the iron center which forces one of the (bulky) chloride ligands in case of iron to dissociate from the metal center upon coordination of the $L_1^H$ ligand. However, as we will show later, a hexacoordinate geometry of the iron(+II) complex with $L_1^H$ is possible if the auxiliary ligands do not occupy much space (e. g. the rod-shaped acetonitrile ligand).

Subsequently, we explored the coordination of FeCl$_2$ to the PP$_3$ ligands $L_1^{CF_3}$, $L_1^{OMe}$ $L_2^H$, and $L_3^{iPr}$ in the presence of NaBF$_4$ (Figure 6). The latter ligand was prepared by reacting the lithium salt of tris-2-(3-methylindolyl)phosphine\cite{38} with chlorodisopropylphosphine, the other ligands were prepared as reported in Chapter 3 and Chapter 4. When the other ligands were coordinated to iron in a similar fashion as for the [FeCl$L_1^H$][BF$_4$] complex, no full conversion was observed as indicated by the presence of free ligand in the filtrate in the $^{31}$P-NMR spectrum. The addition of excess NaBF$_4$ to the purple to pink reaction mixtures nor the addition of alcohol as a co-solvent did increase the yields of
the product significantly.\textsuperscript{[10,16,36]} The CSI mass spectrometry analysis of these reaction mixtures shows the presence of the \([\text{FeClL}]^+\) cation, which indicates that the ligand does coordinate to the iron center. Analysis of the negative ions showed the presence of the expected \(\text{BF}_4^-\) anion but also the presence of the \(\text{FeCl}_3^-\) and \(\text{FeCl}_4^-\) anions. These tetrachlorido ferrates are likely formed from the iron precursor similar as observed for the cobalt and nickel analogues, which is the reason that the reactions do not go to full conversion. When the purple reaction mixture from the reaction of \(\text{L}_3^{\text{iii}}\text{Pr}\) with \(\text{FeCl}_2\) in the presence of \(\text{NaBF}_4\) was dissolved in dichloromethane and layered with pentane, crystals suitable for X-ray diffraction analysis formed. The crystal structure indeed possesses the (oxidized) tetrachlorido ferrate anion, \([\text{FeCl}_4^-]\), as counter ion forming the dimeric \([\text{FeClL}_3^{\text{iii}}\text{Pr}]_2[\text{FeCl}_4^-_2\text{Cl}_4^-_2]\) complex (Figure 8). Tetrachlorido ferrates are very air sensitive, and oxidization likely occurred during workup of the reaction mixture. \([\text{FeClL}_3^{\text{iii}}]\_2[\text{FeCl}_4^-_2\text{Cl}_4^-_2]\) crystallizes as two independent molecules (next to the tetrachlorido ferrate) with almost identical bond angles and distances. They both have a trigonal bipyramidal geometry (\(\tau_{5\#1} = 0.95\) and \(\tau_{5\#2} = 0.98\)) (Table 1).\textsuperscript{[30]} The P1–Fe1, P2–Fe1 and P3–Fe1 bond distances are elongated compared to the \([\text{FeClL}_1^{\text{iv}}]\) unit, which is likely a result of the more electron-donating diisopropylphosphine groups. The other dihedral angles and distances are comparable to the \([\text{FeClL}_1^{\text{iv}}]\) unit and values reported in literature.\textsuperscript{[11,16,36]}

In the context of dinitrogen reduction, the presence of tetrachlorido ferrates as counter ions is undesired, as iron chlorides are active catalysts for dinitrogen reduction, and thus their presence may give false positives.\textsuperscript{[39,40]} In addition, as tetrachlorido ferrates are oxygen sensitive, mixtures of \(\text{Fe(+II)Cl}_4\) and \(\text{Fe(+III)Cl}_4\) may be present as counter ion, which makes stoichiometric reduction to form the iron(0) complex impossible. Therefore,
a different method to form iron complexes was explored. In 2012, the group of Beller described a new method for the coordination of their tripodal tris(2-(diphenylphosphino)phenyl)phosphine (PPh$_3$PPh$_2$) to iron using the Fe(BF$_4$)$_2$, salt as the iron precursor.$^{[4]}$ The coordination of PPh$_3$PPh$_2$ to Fe(BF$_4$)$_2$ led to the formation of the [FeF(PPh$_3$PPh$_2$)][BF$_4$] complex, where the fluoride ligand originates from one of the BF$_4^-$ anions as was evidenced from the crystal structure. The group of Gonsalvi also reacted Fe(BF$_4$)$_2$ with the tetradentate 1,4,7,10-tetraphenyl-1,4,7,10-tetraphosphaadamantane (P$_4$) ligand, but found that the BF$_4^-$ anion stayed intact upon coordination. An Fe(η$^1$-BF$_3$)P$_4$ complex was proposed, where the BF$_4^-$ anion is weakly binding to the iron center.$^{[41]}$ As we anticipated that the formation of tetrachlorido ferrate counter ions would be suppressed using this method, we investigated the coordination of L$_1^H$ with iron precursor Fe(BF$_4$)$_2$ (Figure 9).

![Figure 9](image.png)

**Figure 9:** Reaction of L$_1^H$ and Fe(BF$_4$)$_2$, forming a purple solid that could not be identified. When the purple solid was dissolved in acetonitrile, a color change to orange was observed yielding the [Fe(MeCN)$_2$L$_1^H$][BF$_4$]$_2$, complex.

Stoichiometric amounts of L$_1^H$ and Fe(BF$_4$)$_2$ were stirred in 20 mL 1:1 (v/v) THF/toluene and heated at 70 °C for three days. Unfortunately, no full conversion was reached as indicated by the presence of free ligand in the $^3$P-NMR spectrum of the reaction mixture. However, a purple powder did precipitate from the solution. We were unable to identify the nature of this purple solid as the solid was very oxygen sensitive, paramagnetic and poorly soluble in THF-d$_8$. However, dissolution of the purple solid in acetonitrile caused an immediate color change from purple to orange. This orange solution was diamagnetic as evidenced by $^3$P-NMR spectroscopy, which indicates that the coordination environment around the
metal center has changed. The $^{31}$P-NMR spectrum shows a similar splitting pattern as for the octahedral ruthenium(+II), RuCl$_2$L$_1$$^{II}$, complex (Chapter 3 and 4): an integral-ratio of i (116.77 ppm, dt) : 2 (97.59 ppm, t) : 1 (56.18 ppm, dt), indicating formation of an octahedral geometry around the metal center. CSI mass spectrometry analysis of the orange solution in acetonitrile gave a very clean mass spectrum, representing the [FeFL$_1$$^{III}$]$^+$ cation and the [FeL$_1$$^{III}$]$^{2+}$ di-cation. Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of methanol to an acetonitrile solution of the orange iron complex. The crystal structure possesses two independent molecules in the crystal structure, which indeed show both an octahedral geometry around the metal center of the [Fe(MeCN)$_2$L$_1$$^{II}$][BF$_4$]$_2$ complex (Figure 10). The two cis vacant sites in this crystal structure are occupied by two acetonitrile ligands, rather than a fluorido ligand. The P1–Fe1–P2 angle is 163.17(3)$^\circ$, the P3–Fe1–N4 angle is 177.49(7)$^\circ$, and the P4–Fe1–N5 angle is 175.49(7)$^\circ$, which are all close to the theoretical 180$^\circ$ angle for an ideal octahedral geometry. The P1–Fe1 bond (2.3795(8) Å) is slightly longer than the other P$_{eq}$–Fe bonds (2.2576(8) Å and 2.2494(8) Å), and the axial acetonitrile ligand (N5–C66–C67), seems to bend in the direction of the P1–Fe1 bond.

Figure 10: ORTEP drawing of [Fe(MeCN)$_2$L$_1$$^{II}$]$^+$ (50% probability ellipsoids) showing a side view (left) and bottom view (right) of one of the independent complexes. Hydrogen atoms, solvent molecules and BF$_4^-$ counter ions have been omitted for clarity.

It seems that the observation of the [FeFL$_1$$^{III}$]$^+$ with mass spectrometry was a result of the fluoride transfer reaction between the [FeL$_1$$^{II}$]$^{2+}$ di-cation and the BF$_4^-$ anion in the mass spectrometer. However, the formation of small amounts of [FeFL$_1$$^{III}$]BF$_4$ during coordination of L$_1$$^{II}$ to Fe(BF$_4$)$_2$ in analogy to the formation of Beller’s [FeF(PP$_3$)][BF$_4$] cannot be excluded. Attempts to synthesize iron(+II) complexes with ligands L$_1$CF$_3$ and L$_1$OMe, provide only very low yield of the targeted compounds and therefore this method could unfortunately not be used for the coordination of iron to the other PP$_3$ ligands.
Section 2: Reduction of the cobalt, nickel and iron complexes in presence of N_2

Having the new iron, cobalt and nickel complexes in hand we decided to investigate the behavior of these complexes upon reduction in the presence of dinitrogen. One could expect that in analogy to ruthenium, the iron complexes should bind N_2 upon two electron-reduction to form the respective pentacoordinate 18 VE iron(0) complexes. However, for the cobalt and nickel complexes the coordination of dinitrogen would likely require dissociation of one of the ligand arms for the complexes to adhere to the 18 VE rule. To evaluate whether the dinitrogen complexes can be formed we conducted cyclic voltammetry (CV) studies and in situ reduction of the new complexes in the presence of N_2.

Reduction of [CoClL1][BF_4]

In order to gain insight in the reduction potentials needed for the cobalt complexes to form the Co^0N_2 complex, the [CoClL1][BF_4] complex was analyzed electrochemically. The CV of this cobalt complex shows one reversible reduction-oxidation peak (E^0_\text{1/2} = –0.56 V vs Fc/Fc^+) (see experimental section, Figure 17). This value is slightly more negative than for the reversible Rh^{II}/Rh^I couple of the rhodium [RhClL1][PF_6] analogue (E^0_\text{1/2} = –0.4 V vs Fc/Fc^+)\(^\text{[31]}\), and comparable to the reversible Co^{II}/Co^I couple of the [Co(PPPh_3)(CH_3CN)] [(BF_4)_2] complex (E^0_\text{1/2} = –0.54 V)\(^\text{[42]}\). Therefore, it is likely that reduction-oxidation wave corresponds to the one-electron-reduction of [CoClL1][BF_4] to CoClL1^\text{II}. Scanning to lower potentials resulted in two non-reversible reduction peaks at very similar potentials (E = ± -2.3 and -2.4 V vs Fc/Fc^+). Likely, one of these peaks corresponds to the reduction of Co^I/Co^0, which could lead to binding of the dinitrogen to the cobalt center. Consequently, we also tried to reduce the [CoClL1][BF_4] complex chemically. The chemical reduction of the [CoL1][BF_4] complex with 2 equiv. of KC_8 in the presence of N_2 was monitored by IR spectroscopy. The IR spectra did not show a signal corresponding to the dinitrogen stretch frequency typical for an N_2 coordination complex (Figure 11 and Table 2).
addition, in situ analysis of the reaction mixture by $^{31}$P-NMR spectroscopy showed signals indicative of ligand decomposition. Ligand decomposition may be responsible for the second reduction peak observed in the CV ($E = \pm -2.4$ V vs Fc/Fc$^+$). The inability of the complex to form N$_2$-coordinated complexes may be related to the strong coordination of the ligand, inhibiting the dissociation of one of the phosphine arms when it is bound to cobalt(0).

**Reduction of [NiClL$_1$H][BF$_4$]**

![Figure 12: Reduction of [NiClL$_1$H][BF$_4$] with KC$_8$ under N$_2$ atmosphere.](image)

We also investigated the reduction potentials of the nickel complexes using electrochemistry (see experimental section, Figure 18). Similar as for the cobalt analogue, the CV shows one reversible reduction-oxidation peak at $E^{\circ}_{1/2} = -1.0$ V vs Fc/Fc$^+$ V. In addition, two non-reversible reduction peaks were observed ($E = -2.0$ V vs Fc/Fc$^+$ and $E = -2.5$ V vs Fc/Fc$^+$). Electrochemistry performed with ([Ni(PPh$_3$)(CH$_3$CN)](BF$_4$)$_2$), only led to one reversible reduction-oxidation wave ($E^{\circ}_{1/2} = -1.03$ V vs Fc/Fc$^+$; likely the Ni(+II/+I) couple) and one non-reversible reduction peak, ($E^{\circ}_{1/2} = -1.28$ V vs Fc/Fc$^+$; likely the Ni(+I/0) couple). The chemical reduction of our [NiL$_1$H][BF$_4$] complex with two equivalents of KC$_8$ resulted in a yellow precipitate (Figure 12 and Table 2). Unfortunately, we were unable to measure $^{31}$P-NMR or infrared spectra of this yellow precipitate, as the complex is insoluble in both THF and benzene. The filtrate of the reaction mixture did not show a peak corresponding to an N$_2$ ligand bound to nickel, as indicated by the infrared and $^{31}$P-NMR spectra (Table 2). In literature, a similar yellow solid was observed upon two electron-reduction of similar nickel(+II)PP$_3$ complexes. A dimeric [NiP$_3$]$_2$ complex was postulated, which is formed as a result of the breaking of a nickel-phosphorus bond as was supported by $^1$H-NMR, $^{31}$P-NMR spectroscopy and elemental analysis. Likely, the formed yellow solid upon two electron-reduction of the [NiL$_1$H][BF$_4$] complex is a similar nickel(0) adduct, however, the exact nature remains unclear. Comparable to the cobalt analogue, this result likely indicates that the ligand does not facilitate dinitrogen coordination when bound to nickel(0).
Next, we investigated if it was possible to reduce the \([\text{FeClL}_1\text{H}][\text{BF}_4]\) complex electrochemically. The cyclic voltammogram (see experimental, Figure 19) of \([\text{FeClL}_1\text{H}][\text{BF}_4]\) in THF shows two reversible reduction-oxidation waves at \(E^{0}_{1/2} = -0.38\) V vs \(\text{Ag}^+/\text{AgCl}\) \((-0.96\) V vs \(\text{Fc}/\text{Fc}^+)\) and \(E^{0}_{1/2} = -1.29\) V vs \(\text{Ag}/\text{AgCl}\) \((-1.9\) V vs \(\text{Fc}/\text{Fc}^+)\), corresponding to the \(\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}\) and \(\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}}\) couple respectively. The latter \(\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}}\) reduction potential is much lower compared to the earlier mentioned paramagnetic \([\text{FeClP}_\text{ph}_3^{-}\text{H}]\) complex of Bianchini \((E^{0}_{1/2} = -0.64\) V vs \(\text{Ag}/\text{AgCl})\).[13] Like Bianchini’s complex, the reduction of \(\text{Fe}^{\text{I}}\) to \(\text{Fe}^{\text{0}}\) likely takes place very close to the reduction wave of THF, and can therefore not be determined. From this data is was not apparent if we would be able to reduce the \([\text{FeClL}_1\text{H}][\text{BF}_4]\) complex chemically and bind dinitrogen to the metal center. The addition of two equivalents of \(\text{KC}_8\) in the presence of \(\text{N}_2\) led to the formation of the \(\text{FeN}_2\text{L}_1\text{H}\) complex as indicated by the \(\text{N}_2\) stretch frequency observed in the IR spectrum (Figure 13 and Table 2). Encouraged by this result we also attempted to reduce the other iron complexes with \(\text{KC}_8\) (Figure 14).

**Reduction of other iron(+II)ClPP$_3$ complexes**

The iron(0)\(\text{N}_2\text{PP}_3\) complexes all showed coordination of dinitrogen to the iron metal center, upon two electron-reduction of the corresponding iron(+II) complexes (Table 2). The \(\text{FeN} \_2\text{L}_2\) complex has the highest IR stretch frequency \((\nu = 2068\) cm$^{-1}$) and \(\text{FeN} \_2\text{L}_3^{\text{av}}\) has the lowest IR stretch frequency \((\nu = 2018\) cm$^{-1}$) in the infrared spectrum. These stretch frequencies are in the same order of magnitude as for the tripodal iron \(\text{N}_2\) complexes of Peters *et al.*, which are active catalysts for \(\text{N}_2\) reduction to form ammonia.[20,43,44] The same authors showed that the addition of another equivalent of \(\text{KC}_8\) to the neutral \(\text{FeN} \_2\text{L}\) complexes led to the formation of the negatively charged \([\text{FeN} \_2\text{L}]^{-}\) complex, resulting in higher activation of the \(\text{N}_2\) bond, and better performance in catalysis compared to the neutral iron dinitrogen complex. Unfortunately, the addition of one extra equivalent of \(\text{KC}_8\) to the iron(0)\(\text{N}_2\text{PP}_3\) led to the detection of decomposed ligand in the $^{31}\text{P}$-NMR spectra. In addition, no new peaks corresponding to the \(\text{N}_2\) stretch frequency were detected in the infrared spectrum and the reaction mixtures were also not EPR active. This led us to conclude that the putative negatively charged complexes are too unstable to be detected or not formed at all.
All of the reaction mixtures that were prepared for the \textit{in situ} analysis of the \( \text{N}_2 \) stretch frequency with infrared spectroscopy were set for crystallization by slow diffusion evaporation with pentane. In the case of \( \text{FeClL}_1 \), \( \text{FeClL}_2 \) and \( \text{FeClL}_3 \), crystals suitable for X-ray diffraction were obtained (Figure 15). In all three cases, analysis of the crystal structure showed the presence of the \( \text{FeL}_1 \) complex, indicating that the reduction reaction forming \( \text{Fe}^{0} \text{N}_2 \text{L} \) was not fully completed towards the iron(0) complex. As expected for a d\(^7\) metal complexes, all three iron(+I) complexes feature a distorted trigonal bipyramidal geometry around the metal center due to the Jahn-Teller effect: \( \text{FeClL}_1 \) \( (\tau_5 = 0.75) \), \( \text{FeClL}_2 \) \( (\tau_5 = 0.69) \) and \( \text{FeClL}_3 \) \( (\tau_5 = 0.75) \) (Table 3).
Upon addition of more KC\textsubscript{8} to the [FeCl\textsubscript{L1}H][BF\textsubscript{4}] complex, a more intense absorption in the N\equiv N IR spectrum was observed. When this red reaction mixture was set for crystallization by layering with pentane, crystals suitable for X-ray diffraction analysis formed corresponding to the anticipated FeN\textsubscript{2}L\textsubscript{1}H complex (Figure 16). The crystal structure of FeN\textsubscript{2}L\textsubscript{1}H is a perfect example of a trigonal bipyramidal geometry around the metal center ($\tau_5 = 0.95$)$^{[30]}$. The structure is more symmetrical than the iron(+II) and ruthenium(0) (Chapter 3) analogues, but structurally very comparable to the known FeN\textsubscript{2}(PP\textsubscript{iPr}$_3$) ($\nu_{\text{N}=\text{N}} = 1985$ cm$^{-1}$) complex.$^{[16]}$ The N≡N bond distance of FeN\textsubscript{2}L\textsubscript{1}H is slightly shorter (1.118(5) Å) compared to FeN\textsubscript{2}(PP\textsubscript{iPr}$_3$) (1.1279(16) Å), which is in accordance with a less activated N\equiv N stretch frequency of FeN\textsubscript{2}L\textsubscript{1}H. Thus, these iron-dinitrogen complexes, show observable electronic effects in the N≡N stretch frequency as a result of ligand modifications.

**Figure 15:** ORTEP drawing of FeCl\textsubscript{L1}H (top left), FeCl\textsubscript{L2}H (top right) and FeCl\textsubscript{L3}Pr (bottom) (50% probability ellipsoids). Hydrogen atoms and solvent molecules have been omitted for clarity.
Table 3: Selected bond distances of the FeCl\textsubscript{L1}\textsuperscript{H}, FeCl\textsubscript{L2}\textsuperscript{H}, FeCl\textsubscript{L3}\textsuperscript{ipr} and FeN\textsubscript{2}L\textsubscript{1}\textsuperscript{H} complexes.

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Figure 16: ORTEP drawing of FeN\textsubscript{2}L\textsubscript{1}\textsuperscript{H} (50% probability ellipsoids) showing a side view (left) and bottom view (right). Hydrogen atoms and solvent molecules have been omitted for clarity.
5.3 Conclusions

In conclusion, we have shown that the coordination of iron(+II), cobalt(+II) and nickel(+II) to several tripodal 3-methylindole phosphine based ligands, resulted in the formation of the corresponding cationic metal(+II) complexes. All of the complexes featuring the bulky chloride ligand are five coordinate, with a non-coordinating counterion, which can be either BF$_4^-$ or MCl$_4$. In addition, one octahedral iron PP$_3$ complex was prepared, which features two rod shaped acetonitrile ligands in cis position. The crystal structures obtained give clear insight in the coordination geometry around the metal centers, which is dependent on the number of d-electrons of the metal: a (distorted) trigonal bipyramidal geometry, where the cobalt complex is the most distorted as a result of a Jahn-Teller effect. The geometry of the nickel complex is more distorted than the iron, which is likely a result of the smaller atomic radius of the nickel atom compared to iron atom. The two-electron-reduction of the cobalt(+II) and the nickel(+II) complex in the presence of N$_2$ did not lead to the coordination of N$_2$. However, two-electron-reduction of the iron(+II) complexes did lead to coordination of dinitrogen to the iron center. The corresponding iron-dinitrogen complexes showed observable electronic effects in the N≡N stretch frequency as a result of the ligand modifications: FeN$_2$L$_2^i$I$_P$r$_P$ has the highest IR stretch frequency ($\nu_{N_2} = 2068$ cm$^{-1}$) and FeN$_2$L$_3^{iFi}$ has the lowest IR stretch frequency ($\nu_{N_2} = 2018$ cm$^{-1}$) in the infrared spectrum. The coordination of dinitrogen to the iron(0) PP$_3$ complexes is promising result for the potential application of these complexes as dinitrogen reduction catalysts, as the coordination of dinitrogen to the metal center is the first step in dinitrogen reduction to ammonia.

5.4 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 Et$_2$O were distilled from sodium benzophenone ketyl, CH$_2$Cl$_2$ was distilled from CaH$_2$ under nitrogen. NMR spectra ($^1$H, $^{31}$P, and $^{13}$C{H, $^{31}$P}) 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. L$_1^{ii}$ and L$_2^{ii}$ were prepared in two steps from 3-methylindole.$^{[31-46]}$ L$_1^{CP}$
and \( \text{L}1^{10}\text{Me} \) were prepared as described in Chapter 4 reacting the deprotonated tris-2-(3-methylindolyl)phosphine with the corresponding chlorophosphine in THF at \(-78^\circ\text{C}\). \( \text{KC}_8 \) was prepared by the method of Rabinovitz yielding a finely dispersed brown powder and also ordered from Strem Chemicals Inc, which were bigger golden particles. Experimental X-band EPR spectra were recorded on a Bruker EMX spectrometer equipped with a He temperature control cryostat system (Oxford Instruments).

### Synthesis of new compounds

**Tris-2-(3-methyl-N-diisopropylphosphinoindolyl)phosphine** (\( \text{L}3^{\text{iPr}} \)): Tris-2-(3-methylindolyl)phosphine (1.02 g; 2.42 mmol; 1.0 eq) was dissolved in THF (50 mL) and cooled to \(-78^\circ\text{C}\). n-BuLi (2.5 M in hexanes; 2.9 mL; 7.38 mmol; 3.0 eq) was added dropwise and stirred for 1 hour leaving a yellow solution. Subsequently, chlorodiisopropylphosphine (1.2 mL; 7.38 mmol; 3.0 eq) was added dropwise and stirred for 3 days allowing the reaction mixture to warm to room temperature. The yellow solution was evaporated to dryness, dissolved in \( \text{CH}_2\text{Cl}_2 \) (3 x 10 mL), filtered over basic alumina and evaporated \textit{in vacuo}. The solid was washed with \( \text{Et}_2\text{O} \) (3 x 1 mL), yielding the product in pure form as a white powder (0.83 g; 45% yield). 1H{31P} NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.51 (d, \( J = 16.4 \text{ Hz} \), 3H), 7.49 (d, \( J = 15.8 \text{ Hz} \), 3H), 7.21 (m, 6H) 2.93 - 2.61 (m, 6H), 1.90 (s, 9H), 1.24 (d, \( J = 6.9 \text{ Hz} \), 9H), 1.11 (d, \( J = 7.0 \text{ Hz} \), 9H), 0.88 (d, \( J = 6.8 \text{ Hz} \), 9H), 0.46 (d, \( J = 6.9 \text{ Hz} \), 9H) ppm. 31P-NMR (121 MHz, CDCl\(_3\)): \( \delta \) 63.35 (d, \( J = 168.7 \text{ Hz} \), 3P), –77.94 (q, \( J = 168.8 \text{ Hz} \), 1P). 13C{1H,31P}-NMR (75 MHz, CDCl\(_3\)): \( \delta \) 140.90, 137.14, 133.30, 123.64, 122.19, 119.51, 118.95, 112.98, 27.19, 26.51, 21.85, 21.31, 20.18, 19.44, 10.03 ppm.

**[FeClL1H][BF4]**: L1H (1.05 g; 1.08 mmol; 1.0 eq), NaBF\(_4\) (150 mg; 1.18 mmol; 1.1 eq) and FeCl\(_2\) (118 mg; 1.08 mmol; 1.0 eq) were suspended in THF (40 mL) and stirred overnight. The purple reaction mixture was evaporated \textit{in vacuo} and extracted with \( \text{CH}_2\text{Cl}_2 \) (100 mL). The purple solution was filtered, evaporated \textit{in vacuo}, dissolved in THF (3 x 10 mL) and evaporated to dryness to remove the residual \( \text{CH}_2\text{Cl}_2 \). The solid was washed with \( \text{Et}_2\text{O} \) (3 x 5 mL) and dried \textit{in vacuo} yielding the complex as a purple solid. Yield: 404.2 mg (35%) ± half of the amount of solid was lost during the work up. Crystals suitable for X-ray diffraction analysis were obtained by layering a dichloromethane solution of FeClL1HBF\(_4\) with pentane. 1H-NMR (300 MHz, CDCl\(_3\)): \( \delta \) 16.24 (bs), 14.74 (bs), 8.87 (bs), 8.35 (bs), 3.13 (bs), –0.37 (bs), –8.30 (bs), –9.14 (bs). UV-Vis (THF) \( \lambda_{\text{max}} \): 553 nm\(^{-1}\). Mass Analysis (CSI) [FeClL1H]: found: 1064.2105 calc: 1064.2105; [BF\(_4\)]: found: 87.0000, calc: 87.0029.
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**[CoClL1H][BF₄] : L1H (115.3 mg; 0.12 mmol; 1.0 eq), NaBF₄ (11.3 mg; 0.10 mmol; 1.0 eq) and CoCl₂·6H₂O (113 mg; 0.12 mmol; 1.0 eq) were suspended in THF (10 mL) and stirred overnight. The brown precipitate was filtered off and washed with Et₂O. Subsequently the solid was dried in vacuo yielding the complex as a brown solid. Yield: 110.3 mg (0.095 mmol, 92.8 %). Mass Analysis (CSI) [CoClL1H-H]: found: 1067.2092 calc: 1067.2054; [BF₄]: found: 87.0012, calc: 87.0029.**

**[CoClL1H][CoCl₄]: L1H (103.4 mg; 0.11 mmol; 2.0 eq) and CoCl₂·6H₂O (43.6 mg; 0.16 mmol; 3.0 eq) were suspended in THF (10 mL) and stirred overnight. Pentane was added until all of the complex had crashed out. This brown solid was filtered off, washed with pentane and dried in vacuo yielding the complex as a brown solid. Yield: 108.4 mg (0.046 mmol, 87.4 %). Layering of a dichloromethane solution of [CoClL1H][CoCl₄] with pentane resulted in crystals suitable for X-ray diffraction analysis. Mass Analysis (CSI) [CoClL1H-H]: found: 1067.2092 calc: 1067.2054; ([CoClL1H][CoCl₃]) : found: 2302.2782, calc: 2302.2511; [CoCl₃]: found: 163.8409, calc: 163.8398.**

**[NiClL1H][BF₄]: L1H (94.9 mg; 0.097 mmol; 1.0 eq), NaBF₄ (10.7 mg; 0.097 mmol; 1.0 eq) and NiCl₂·6H₂O (23.1 mg; 0.097 mmol; 1.0 eq) were suspended in THF (10 mL) and stirred overnight. The green precipitate was filtered off and washed with Et₂O. Subsequently the solid was dried in vacuo yielding the complex as a brown solid. Yield: 98.9 mg (0.086 mmol, 87.9 %). **¹H-NMR (300 MHz, CDCl₃) δ: 7.81 (d, J = 8.1 Hz, 3H), 7.27 - 7.17 (m, 9H), 7.12 - 6.82 (m, 29H), 6.29 (d, J = 8.5 Hz, 3H), 2.67 (s, 9H). **³¹P-NMR (121 MHz, CDCl₃): δ 61.06 (d, J = 47.1 Hz, 3P), 25.91 (q, J = 47.4 Hz, 1P). **¹³C{¹H,³¹P}-NMR (75 MHz, CDCl₃) δ: 139.65 (m, C₆), 136.03(m, C₆), 130.94 (s, CH-ph), 130.02 (m, CH-ph), 128.99 (m, CH-ph), 126.99 (s, CH-ind), 123.57(s, CH-ind), 122.27(s, CH-ind), 115.78 (s, CH-ind), 10.69 (s, CH₃) ppm. Mass Analysis (CSI) [NiClL1H-H]: found: 1066.2097 calc: 1066.2075; [BF₄]: found: 87.0049, calc: 87.0029.**
[NiClL₁H₂][NiCl₄]: L₁H (104.1 mg; 0.11 mmol; 1.0 eq) and NiCl₂ · 6 H₂O (38.2 mg; 0.16 mmol; 1.0 eq) were suspended in THF (10 mL) and stirred overnight. Pentane was added until all of the complex had crashed out. The green precipitate was filtered off and washed by Et₂O. Subsequently the solid was dried in vacuo yielding the complex as a green solid. Yield: 94.3 mg (0.041 mmol, 76.8 %).

1H-NMR (300 MHz, CDCl₃) δ: 7.81 (d, J = 8.1 Hz, 3H), 7.27 - 7.17 (m, 9H), 7.12 - 6.82 (m, 29H), 6.29 (d, J = 8.5 Hz, 3H), 2.67 (s, 9H).

31P-NMR (121 MHz, CDCl₃): δ 61.06 (d, J = 47.1 Hz, 3P), 25.91 (q, J = 47.4 Hz, 1P).

Slow diffusion evaporation of hexane to a dichloromethane solution of [NiClL₁H₂][NiCl₄] resulted in the formation of crystals suitable for X-ray diffraction analysis. Mass Analysis (CSI) [NiClL₁H₂-H]: found: 1066.2097 calc: 1066.2075; negative: no fragments belonging to the complex could be observed.

[FeClL₃iPr₂][BF₄]ₓ[FeCl₄]ₓ: L₃iPr (0.523 g; 0.68 mmol; 1.0 eq), NaBF₄ (0.082 g; 0.74 mmol; 1.1 eq) and FeCl₂ (0.178 g; 1.36 mmol; 2.1 eq) were suspended in THF (10 mL) and stirred for three days. The reaction mixture was evaporated to dryness, washed with pentane (5 x 10 mL) and extracted with CH₂Cl₂ (100 mL). The purple solution was filtered, evaporated in vacuo, dissolved in THF (3 x 10 mL) and evaporated in vacuo to remove the residual CH₂Cl₂. After washing with Et₂O and drying in vacuo the solid was obtained as a paramagnetic purple powder. Yield: not determined. Crystals were prepared by layering a dichloromethane solution with pentane at 5 °C. CSI mass analysis showed that the product was a mixture of [FeClL₃iPr₂][BF₄]ₓ[FeCl₄]ₓ, but the exact ratio could not be determined. Mass Analysis (CSI) [FeClL₃iPr₂]: found: 860.2963 calc: 860.3012. [BF₄]: found: 87.0049; [FeCl₃]: found: 160.8455; [FeCl₄]: 197.8139.

Reactions of L₁OMe, L₁CF₃ and L₂H with FeCl₂ were performed in a similar way as [FeClL₃iPr₂][BF₄]ₓ[FeCl₄]ₓ leading to mixtures of the [FeClL]⁺ with unknown amounts of BF₄ and FeCl₄. These mixtures were used as such for the reduction to the FeN₂L complex and the in situ analysis of the N₂ stretch frequency using infrared spectroscopy.

Reaction of L₁H with Fe(BF₄)₂: L₁H (488 mg 0.5 mmol) and Fe(BF₄)₂ · 6 H₂O (168 mg, 0.5 mmol) were suspended in 20 ml 1:1 (v/v) THF/toluene and heated at 70 °C for three days. The purple precipitated complex was filtered off and dried in vacuo to yield 369.2 mg of a purple solid. When the purple solid was dissolved in acetonitrile, a color change to orange was observed, yielding [Fe(MeCN)₂L₁H][BF₄].
[Fe(MeCN)$_2$L$_1$H][BF$_4$]$_2$; a solution of the purple powder obtained in the previous procedure in acetonitrile was set for crystallization by slow diffusion evaporation of methanol at 5°C resulting in the formation of crystals suitable for X-ray diffraction analysis. $^1$H-NMR (300 MHz, CD$_3$CN) δ: broad peaks as a result of paramagnetic impurities: 7.80, 7.42, 7.39, 7.16, 6.85, 6.57, 6.37, 5.92, 3.00, 2.70, 2.60, 1.93. $^{31}$P-NMR (121 MHz, CD$_3$CN) δ: 116.77 (q), 97.59 (t, $J = 44.2$ Hz), 56.18 (q). The $^{13}$C-NMR spectrum could not be obtained in pure form. $^{19}$F-NMR (282 MHz, CD$_3$CN) δ: 151.10 ppm. Mass analysis (CSI) [FeL$_1$H-H]$^{2+}$: found: 514.6169, calc: 514.6192; [FeF$_2$L$_1$H]$^+$: found: 1048.2362 calc: 1048.2369; [BF$_4$]$: found: 87.0049, calc: 87.0029

**Standard procedure for the reduction of the complexes with KC$_8$**

± 20 mg of the complex was suspended with 2-5 equivalents of KC$_8$ in 2 mL THF in the glovebox and stirred for 2–3 hours. The solution was filtered and part of the solution was used for in situ infrared spectroscopy, the rest of the solution was set for crystallization by evaporation of pentane vapors to the THF solution. Crystals suitable for X-ray diffraction analysis formed for complexes FeClL$_1$H, FeClL$_2$H, FeClL$_3$H and FeN$_2$L$_1$H. (crystals of FeN$_2$L$_1$H were obtained by layering of the THF solution with pentane).
Cyclic Voltammetry

Cyclic voltammograms of the complex \((10^{-3} \text{ M})\) were measured in deaerated THF in the presence of Bu₄NPF₆ \((0.1 \text{ M})\); \(\nu = 0.1 \text{ V s}^{-1}\); glassy carbon working electrode, platinum counter electrode, silver reference electrode.

\[\text{Potential vs Fc/Fc}^+ [\text{V}]\]

**Figure 17:** CV of [CoL1][BF₄] showing one reversible reduction-oxidation peak \((E^{0}_{\text{red}} = -0.56 \text{ V vs Fc/Fc}^+)\) and two non-reversible reduction peaks at very close proximity to another \((E = \pm -2.3 \text{ and } -2.4 \text{ V vs Fc/Fc}^+)\).
Figure 18: CV of [NiL1][BF₄] showing one reversible wave ($E_{1/2}^{0} = -1.0 \text{ V vs Fc/Fc}^+$) and two non-reversible waves ($E = -2.0 \text{ V vs Fc/Fc}^+$ and $E = -2.5 \text{ V vs Fc/Fc}^+$).

Figure 19: CV of [FeClL1][BF₄]. $E_{1/2}^{0} = -0.96 \text{ V vs Fc/Fc}^+$ and $E_{1/2}^{0} = -1.9 \text{ vs Fc/Fc}^+$. 
### X-ray diffraction analysis data

Table 4: Crystallographic data for 

<table>
<thead>
<tr>
<th>Compound</th>
<th>Empirical formula</th>
<th>FW</th>
<th>Temperature [K]</th>
<th>Radiation</th>
<th>Wavelength [Å]</th>
<th>Cryst. syst.</th>
<th>Space group</th>
<th>(a) [Å]</th>
<th>(b) [Å]</th>
<th>(c) [Å]</th>
<th>(\alpha) [deg]</th>
<th>(\beta) [deg]</th>
<th>(\gamma) [deg]</th>
<th>Volume [Å(^3)]</th>
<th>Z</th>
<th>Color</th>
<th>(\theta)-max</th>
<th>Density [Mg m(^{-3})]</th>
<th>Absorp. Coeff. [mm(^{-1})]</th>
<th>(F(000))</th>
<th>(R_1)/wR(_2)/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CoCl(_2)L(_1)H]_2[CoCl(_4)]</td>
<td>(2(C_{63}H_{51}ClCoN_3P_4)), Cl(_2)Co, 3(CH(_2)Cl(_2)) [+ solvent]</td>
<td>2592.17(a)</td>
<td>150</td>
<td>Mo K(_\alpha)</td>
<td>0.71073</td>
<td>Triclinic</td>
<td>P-1</td>
<td>13.3337(6)</td>
<td>17.5858(8)</td>
<td>30.2447(14)</td>
<td>80.302(2)</td>
<td>77.747(2)</td>
<td>73.851(2)</td>
<td>6611.5(5)</td>
<td>2</td>
<td>purple</td>
<td>25.215</td>
<td>1.302(a)</td>
<td>0.760(a)</td>
<td>2658.0(a)</td>
<td>0.0568/0.1764/1.224</td>
</tr>
<tr>
<td>[NiCl(_2)L(_1)H]_2[NiCl(_4)]</td>
<td>(2(C_{63}H_{51}ClNiN_3P_4)), 5(CH(_2)Cl(_2)) , Cl(_4)Ni [+ solvent]</td>
<td>2761.30(a)</td>
<td>150</td>
<td>Mo K(_\alpha)</td>
<td>0.71073</td>
<td>Triclinic</td>
<td>P-1</td>
<td>13.3226(5)</td>
<td>17.5159(7)</td>
<td>30.4118(13)</td>
<td>92.763(2)</td>
<td>102.183(2)</td>
<td>105.778(2)</td>
<td>6633.4(5)</td>
<td>2</td>
<td>red-black</td>
<td>25.207</td>
<td>1.383(a)</td>
<td>0.890(a)</td>
<td>2832.0(a)</td>
<td>0.0524/0.1723/1.206</td>
</tr>
<tr>
<td>[FeCl(_2)L(_1)H][BF(_4)]</td>
<td>(C_{63}H_{51}ClFeN_3P_4) , BF(_4) , CH(_2)Cl(_2)</td>
<td>1236.99</td>
<td>150</td>
<td>Mo K(_\alpha)</td>
<td>0.71073</td>
<td>monoclinic</td>
<td>P 2(1)/n</td>
<td>18.7293(11)</td>
<td>14.6035(10)</td>
<td>21.6807(15)</td>
<td>90</td>
<td>103.379(3)</td>
<td>90</td>
<td>5769.0(7)</td>
<td>4</td>
<td>dark purple</td>
<td>25.150</td>
<td>1.424</td>
<td>0.569</td>
<td>2544.0</td>
<td>0.0419/0.1354/0.866</td>
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</table>

\(a\) Excluding the disordered solvent contribution.
Table 5: Crystallographic data for [\(\text{Fe(MeCN)}_2\text{L1}^\text{H}\)]\(\text{[BF}_4\text{]}_2\), \(\text{FeClL1}^\text{H}\) and \(\text{FeClL2}^\text{H}\).

<table>
<thead>
<tr>
<th></th>
<th>[(\text{Fe(MeCN)}_2\text{L1}^\text{H})](\text{[BF}_4\text{]}_2)</th>
<th>(\text{FeClL1}^\text{H})</th>
<th>(\text{FeClL2}^\text{H})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>(2(\text{C}_6\text{H}_7\text{FeN}_5\text{P}_4),)</td>
<td>(\text{C}<em>{63}\text{H}</em>{51}\text{ClFeN}_3\text{P}_4)</td>
<td>(\text{C}<em>{63}\text{H}</em>{51}\text{ClFeN}_3\text{P}_4)</td>
</tr>
<tr>
<td></td>
<td>(4(\text{BF}_4),3(\text{CH}_4\text{O}),) + solvent</td>
<td>(\text{C}_2\text{H}_2\text{O})</td>
<td>(\text{C}_7\text{H}_8)</td>
</tr>
<tr>
<td>FW</td>
<td>2667.19 a</td>
<td>1137.35</td>
<td>1157.38</td>
</tr>
<tr>
<td>Temperature [K]</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Radiation</td>
<td>(\text{Mo K}\alpha)</td>
<td>(\text{Mo K}\alpha)</td>
<td>(\text{Mo K}\alpha)</td>
</tr>
<tr>
<td>Wavelength [Å]</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Cryst. syst.</td>
<td>monoclinic</td>
<td>Triclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>(\text{C 2/c})</td>
<td>(\text{P-1})</td>
<td>(\text{P 21/n})</td>
</tr>
<tr>
<td>a [Å]</td>
<td>62.559(3)</td>
<td>11.9943(4)</td>
<td>12.2673(8)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>13.9074(6)</td>
<td>14.5426(4)</td>
<td>18.0296(12)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>36.4599(17)</td>
<td>17.1360(5)</td>
<td>25.6360(18)</td>
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<tr>
<td>α [deg]</td>
<td>90</td>
<td>83.549(2)</td>
<td>90</td>
</tr>
<tr>
<td>β [deg]</td>
<td>111.113(2)</td>
<td>86.435(2)</td>
<td>93.364(2)</td>
</tr>
<tr>
<td>γ [deg]</td>
<td>90</td>
<td>70.304(2)</td>
<td>90</td>
</tr>
<tr>
<td>Volume [Å³]</td>
<td>29592(2)</td>
<td>2795.37(15)</td>
<td>5660.3(7)</td>
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<tr>
<td>Z</td>
<td>8</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Color</td>
<td>orange</td>
<td>dark red</td>
<td>brown-orange</td>
</tr>
<tr>
<td>θ-max</td>
<td>25.175</td>
<td>25.040</td>
<td>25.086</td>
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<tr>
<td>Density [Mg m\textsuperscript{-3} ]</td>
<td>1.197 a</td>
<td>1.351</td>
<td>1.358</td>
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<tr>
<td>Absorp. Coeff. [mm\textsuperscript{-1} ]</td>
<td>0.353 a</td>
<td>0.480</td>
<td>0.474</td>
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<tr>
<td>(F(000))</td>
<td>11024.0 a</td>
<td>1186.0</td>
<td>2412.0</td>
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<tr>
<td>(R_1) / (wR_2) / (S)</td>
<td>0.0518 / 0.1569 / 1.038</td>
<td>0.0480 / 0.1436 / 0.950</td>
<td>0.0375 / 0.1291 / 0.979</td>
</tr>
</tbody>
</table>

a) Excluding the disordered solvent contribution.
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.\[^{47}\] Multiscan absorption correction and scaling was performed with SADABS.\[^{48}\] The structure was solved with Intrinsic Phasing Methods using SHELXT.\[^{49}\] Least-squares refinement was performed with SHELXL 2013\[^{50}\] 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. The structures of RuCl\(_2\)\(L_1^{H}\) and RuCl\(_2\)\(L_2^{H}\) 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.\[^{51}\]
5.5 References

Chapter 5


[33] The DFT (BP86, SV(P)) calculated energy of the pentet state (HS) and the singlet state (LS) are higher in energy than the triplet state (IS) by 24 kcal/mol and 7.7 kcal/mol respectively.

[34] The DFT (BP86, SV(P)) calculated energy of the pentet state (HS) and the singlet state (LS) are higher in energy than the triplet state (IS) by 24 kcal/mol and 7.7 kcal/mol respectively.


