Coordination of 3-Methylindole-Based Tripodal Tetraphosphine Ligands to Iron(II), Cobalt(II), and Nickel(II) and Investigations of their Subsequent Two-Electron Reduction

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Published in: European Journal of Inorganic Chemistry

DOI: 10.1002/ejic.201701209

Link to publication

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Nitrogen Fixation

Coordination of 3-Methylindole-Based Tripodal Tetraphosphine Ligands to Iron(II), Cobalt(II), and Nickel(II) and Investigations of their Subsequent Two-Electron Reduction


Abstract: We report the coordination chemistry of indole based tripodal tetraphosphine ligands to iron(II), cobalt(II) and nickel(II). These complexes are formed by simple synthetic protocols and were characterized by a combination of spectroscopic techniques and single-crystal X-ray analysis. The molecular structures as determined by X-ray diffraction show that the geometry of the nickel and cobalt complexes are distorted trigonal bipyramidal. The monocationic iron(II) complexes also have distorted trigonal bipyramidal geometries, but the dicationic analogue has an octahedral geometry. Two-electron reduction of the cobalt(II) and the nickel(II) complexes in the presence of N₂ did not lead to the coordination of N₂. In contrast, two-electron reduction of the iron(II) complexes did lead to coordination of dinitrogen to the iron center. The Fe₂N₂L₁H complex has a trigonal bipyramidal geometry, and the N–N bond length of the coordinated dinitrogen ligand is longer than that of free dinitrogen, indicating that coordination to this iron(0) complex results in activation of the N≡N bond.

Introduction

Recent years brought about a renaissance of coordination chemistry of base metals. Their abundance and generally lower toxicity in comparison to noble metals makes them ideal candidates to explore them as new homogeneous catalysts.[1–4] Complexes of base metals with phosphine based ligands are among the many highly active catalysts that can facilitate very challenging reactions ranging from reduction of unsaturated compounds such as alkynes,[5] aldehydes[6] or carboxylic acids and esters[7] to reduction of CO₂.[8–14] In particular, expanding the coordination chemistry of base metals with tripodal, tetradentate ligands is attractive, as complexes of tripodal phosphine ligands with base metal iron and cobalt reveal outstanding activity in (among others) dehydrogenation/hydrogenation of CO₂-based fuels or reduction of N₂.[11,15–19]

We turned our attention to the tripodal, tetradentate tris[1-(diphenylphosphanyl)-3-methyl-1H-indol-2-yl]phosphane ligand (L₁H) (Figure 1), which has previously been used in coordination chemistry with Pd,[20] Rh,[21,22] Cu,[22] and Ru,[23,24] showing a remarkable potential to stabilize rare paramagnetic RhII[20] and RuI species,[23] as well as Ru₀ dinitrogen complexes.[23,24] These intriguing results triggered us to further explore the coordination behavior of the tripodal indolyl-based ligands with the earth abundant metals iron, cobalt and nickel. Tripodal tetradentate phosphine based complexes using either PPh₃ = P(CH₂CH₂PPh₂)₃ or PPr₃ = [P(CH₂CH₂PPr₂)₃] coordinated to iron(II), cobalt(II) and nickel(II) have been exten-
sively studied.\textsuperscript{[25–30]} These tripodal ligands generally occupy four coordination sites around a metal center and a trigonal bipyramidal geometry (TPB) is the most commonly observed geometry when the ligand is coordinated to a first row transition metal center.\textsuperscript{[29,31]} These \([MX(PP_3)]^+\) complexes are formed by reacting the corresponding \(MX_2\) 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.

In this paper, we first discuss the coordination of tripodal indolyl-based tetraphosphine ligands to the first-row late transition metals iron, cobalt, and nickel. The coordination of tris[1-(diphenylphosphanyl)-3-methyl-1H-indol-2-yl]phosphane (\(L_1\)) to these metals is investigated in detail. 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 (\(L_{1H}, L_{2H}\) and \(L_{3PP}\)) 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 described. Electrochemical reduction is used to evaluate if these complexes are redox-active. We further investigate the capability of these complexes to bind \(N_2\) upon two-electron reduction with \(K\text{C}_8\). In addition, we explored whether ligand modification leads to observable electronic effects in the \(N\equiv N\) stretch frequency when the \(PP_3\) 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 the \(\text{iron(II)}\) complexes with ligands \(L_{1H}, L_{2H}\) and \(L_{3PP}\) and iron(0) with ligand \(L_{1H}\).

**Results and Discussion**

**Formation of Mono and Binary Cobalt \(L_{1H}\) Complexes**

We started our investigations with coordination studies of the tripodal indolyl-based tetraphosphine ligand (\(L_{1H}\)) to cobalt(II). Stoichiometric amounts of \(L_{1H}\) and \(CoCl_2\cdot6H_2O\) in THF did not lead to full consumption of \(L_{1H}\) as judged by in situ \(^{31}\text{P}\) NMR spectroscopy. Cold Spray Electron Ionization Mass Spectroscopy (CS-ESI-MS) revealed the presence of \(CoCl_2^{2-}\) dianion which pointed to the possibility of the formation of a pentacoordinate \([Co\text{Cl}_2\text{L}_{1H}]_2[CoCl_4]\) (1a) complex in which a part of the \(CoCl_2\) acts as a chloride scavenger. Formation of tetrachlorido metallates upon coordination of multidentate ligands has been reported for several systems.\textsuperscript{[32–39]} Therefore, we reacted \(L_{1H}\) with \(CoCl_2\) in a 2:3 stoichiometry to quantitatively form the binary \([Co\text{Cl}_2\text{L}_{1H}]_2[CoCl_4]\) complex 1a. The monometallic complex could be obtained when the reaction was carried out in the presence of \(NaBF_4\) (Figure 1) with the sodium cation acting as the scavenger of one of the chloride anions. This led to clean formation of \([Co\text{L}_{1H}]BF_4\) (1b) from stoichiometric amounts of \(L_{1H}\) and \(CoCl_2\cdot6H_2O\) in THF.

CS-ESI mass spectroscopy analysis showed the presence of the \([Co\text{Cl}_2\text{L}_{1H}]^+\) cation in both \([Co\text{Cl}_2\text{L}_{1H}]BF_4\) (1b) and \([Co\text{Cl}_2\text{L}_{1H}]_2[CoCl_4]\) (1a) samples (see experimental section). Similar to findings reported by Braunstein and co-workers the \([Co\text{Cl}_2\text{L}_{1H}]_2[CoCl_4]\) fragment could be detected in the \([Co\text{Cl}_2\text{L}_{1H}]_2[CoCl_4]\) sample, indicating formation of the proposed binary complex.\textsuperscript{[29,40]} Both the cationic and anionic cobalt complexes are paramagnetic. EPR analysis of the \([Co\text{L}_{1H}]BF_4\) (1b) and \([Co\text{Cl}_2\text{L}_{1H}]_2[CoCl_4]\) (1a) complexes in THF at 20 K are indicative for an \(S = 1/2\) system with the cobalt(II) ion being in a low-spin configuration (Figure 2). Small hyperfine couplings (presumably with cobalt and the phosphine atoms) are also noticeable. In addition, the spectrum of \([Co\text{Cl}_2\text{L}_{1H}]_2[CoCl_4]\) shows an extra signal (700–2500 G) corresponding to the high spin tetrachlorido cobaltate anion, which is absent in the \([Co\text{L}_{1H}]BF_4\).

Layering a dichloromethane solution of \([Co\text{Cl}_2\text{L}_{1H}]_2[CoCl_4]\) with pentane resulted in the formation of single crystals suitable for X-ray diffraction analysis (Figure 3). As expected, the binary complex \([Co\text{Cl}_2\text{L}_{1H}]_2[CoCl_4]\) 1a is present in the crystal structure. The two \([Co\text{Cl}_2\text{L}_{1H}]^+\) 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 (\(r_{5\pi1} = 0.55\) and \(r_{5\pi2} = 0.67\))\textsuperscript{[41]} (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) complex \([Rh\text{Cl}_2\text{L}_{1H}]PF_6\) (\(r_5 = 0.55\)).\textsuperscript{[20]} The four strong-field phosphine ligands favor the formation of low spin complexes, thus, \(d^7\) complexes tend to form square pyramidal geometries. As the rigidity of the ligand scaffold does not allow such arrangement, a geometry in-between trigonal bipyramidal and a square pyramid is formed. This is different for the iron(II) and nickel(II) 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 trigonal bipyramidal geometry with this ligand scaffold.
Table 1. Selected bond lengths and angles of the [Co(Cl)L1H](1a) and [Ni(Cl)L1H]2[NiCl4](2a) complexes.

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>[Co(Cl)L1H]+ #1</th>
<th>[Co(Cl)L1H]+ #2</th>
<th>[Ni(Cl)L1H]+ #1</th>
<th>[Ni(Cl)L1H]+ #2</th>
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</thead>
<tbody>
<tr>
<td>M1–P1</td>
<td>2.2422(11)</td>
<td>2.2691(11)</td>
<td>2.2187(10)</td>
<td>2.2562(10)</td>
</tr>
<tr>
<td>M1–P2</td>
<td>2.2590(11)</td>
<td>2.2652(11)</td>
<td>2.2382(10)</td>
<td>2.2548(10)</td>
</tr>
<tr>
<td>M1–P3</td>
<td>2.2673(11)</td>
<td>2.2550(11)</td>
<td>2.3108(10)</td>
<td>2.2772(10)</td>
</tr>
<tr>
<td>M1–P4</td>
<td>2.1432(11)</td>
<td>2.1434(11)</td>
<td>2.1321(10)</td>
<td>2.1290(10)</td>
</tr>
<tr>
<td>M1–Cl1</td>
<td>2.2401(11)</td>
<td>2.2382(11)</td>
<td>2.3339(10)</td>
<td>2.2323(10)</td>
</tr>
<tr>
<td>P1–M1–P2</td>
<td>140.74(4)</td>
<td>137.07(4)</td>
<td>131.39(4)</td>
<td>126.51(4)</td>
</tr>
<tr>
<td>P1–M1–P3</td>
<td>110.35(4)</td>
<td>109.62(4)</td>
<td>116.25(4)</td>
<td>116.47(4)</td>
</tr>
<tr>
<td>P2–M1–P3</td>
<td>107.23(4)</td>
<td>111.12(4)</td>
<td>111.39(4)</td>
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<tr>
<td>C11–M1–P4</td>
<td>173.63(5)</td>
<td>177.33(4)</td>
<td>173.23(4)</td>
<td>177.94(4)</td>
</tr>
</tbody>
</table>

Formation of Mono and Binary Nickel L1H Complexes

Similar to the cobalt system, the coordination of nickel(II) chloride hexahydrate to L1H resulted in the formation of either the [Ni(Cl)L1H][NiCl4](2a) or the [Ni(Cl)L1H]BF4 (2b) complexes, depending on the use of NaBF4 during the synthesis (Figure 1). As expected for the pentacoordinate d8 complexes with strong-field phosphorus ligands, the [Ni(Cl)L1H]+ cations are diamagnetic, and thus NMR analysis of the complexes was possible. The identical 31P NMR spectra of Ni(Cl)L1HBF4 (1b) and [Ni(Cl)L1H][NiCl4] (1a) show one doublet (δ = 61.06 ppm) and one quartet (δ = 25.91 ppm), indicating a C3-symmetrical trigonal bipyramidal geometry in solution (on the NMR time scale). C3-symmetrical diamagnetic complexes of tripodal tetradentate phosphines coordinated to nickel have been previously reported,[29,42,43] and trigonal bipyramidal geometry was also reported for the d8 [Ru(N2)L1H][Cl]23] and the [Pd(Cl)L1H][Cl]22] complexes. Interestingly, whereas the coordination of nickel to L1H results in the formation of the binary [Ni(Cl)L1H][NiCl4] complex 2a, the palladium complex does not form the tetrachlorido palladate, but one of the chloride anions remains non-coordinating.[20] In accordance with the NMR spectroscopic data, CSI mass spectrometry analysis showed the presence of the
Formation of Iron PP₃ Complexes

The above results show that the coordination of the tetradentate indolyl phosphine ligand L₁H to d⁶ nickel(II) and d⁷ cobalt(II) chlorides results in formation of (highly distorted in the case of cobalt) trigonal bipyramidal complexes of the type [M(II)(Cl)L₁H]⁺ and that in the absence of non-coordinating BF₄⁻ anion, binary tetrachlorido metallate complexes are formed. We next turned our attention to iron, and the results of these investigations are described in the following section. Whereas in the case of nickel and cobalt the L₁H ligand complexes are pentacoordinate, complexation of this ligand to d⁷ iron(II) could in principle result in formation of a hexacoordinate 18 VE complex, as was observed for iron’s heavier analogue ruthenium,[12,13] or alternatively in the 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 phosphine ligands. The reaction of FeCl₂ with L₁H and NaBF₄ in THF in a 1:1:1 stoichiometry led to full conversion of the ligand according to the absence of its ³¹P NMR signal, and the formation of a purple, paramagnetic complex as judged by the presence of broad peaks in the ¹H NMR spectrum in the region between 16.3 and 9.1 ppm. The paramagnetic behavior hinted at the formation of a five-coordinate species. CS-ESI mass spectrometry analysis in both positive and negative modes shows the presence of both the [Fe(II)(Cl)L₁H]⁺ cation and the BF₄⁻ counterion respectively, 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 pentacoordinate iron complex [Fe(II)(Cl)L₁H]BF₄ (3b). DFT calculations suggest that the lowest energy state of the [Fe(II)(Cl)L₁H]⁺ cation is an intermediate spin, paramagnetic trigonal bipyramidal complex,[44] iron(II) (d⁵) complexes with TBP geometry that are paramagnetic are not uncommon.[19,28,30,45,46] Crystals suitable for X-ray diffraction were obtained by layering a dichloromethane solution of [Fe(II)(Cl)L₁H]BF₄ (3b) with pentane.

As anticipated, the crystal structure shows a trigonal bipyramidal geometry around the metal center (Figure 5). The overall crystal structural data is in good agreement with other tripodal five-coordinate tetraphosphine TBP iron(II) complexes.[10,11,19,28,37,46] The largest equatorial angle P₁–Fe₁–P₂ of 120.51° (Table 2) fits well with that of an ideal TBP geometry, which is in correspondence with a τ₅ = 0.92.[44]

Subsequently, we explored the coordination of FeCl₂ to the PP₃ ligands L₁CF₃, L₁OMe, L₂H, and L₃PP in the presence of NaBF₄ (Figure 6) to form complexes 4, 5, 6, and 7, respectively. The new ligand L₃PP was prepared by reacting the lithium salt of tris-2-(3-methylindolyl)phosphine[47] with disiropropyl chlorophosphine. Coordination of ligands other than L₁H to iron in presence of NaBF₄ did not provide the monometallic complex [Fe(II)(Cl)L₁H]BF₄ quantitatively as indicated by the presence of free ligand in the filtrate in the ³¹P NMR spectrum. The addition of excess NaBF₄ to the purple to pink reaction mixtures nor the addition of alcohol as a co-solvent increases the yields of the product significantly.[19,27,46]. Nevertheless, the CS-ESI mass spectrometry analysis of these reaction mixtures in the positive mode shows the presence of the [Fe(II)(Cl)L₃]⁺ cation, which indicates that the ligand does coordinate to the iron center. Analy-
sis in the negative mode 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, as was 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 \( \text{L}^3\text{Pr} \) 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 contains the (oxidized) tetrachlorido ferrate anion \( [\text{FeCl}_4^-] \) (likely formed in situ by a reaction of \( [\text{FeCl}_4^2-] \) with traces of oxygen) as counterion, resulting in the binary \( [\text{FeCl}_3\text{Pr}] [\text{FeCl}_4^-] \) complex 7 (Figure 7).

Figure 6. Synthesis of \( \text{L}^3\text{Pr} \) and coordination of \( \text{L}^1\text{CF}_3, \text{L}^1\text{OMe,} \text{L}^3\text{Pr} \) and \( \text{L}^2\text{H} \) to \( \text{FeCl}_2 \) in the presence of \( \text{NaBF}_4 \).

Figure 7. Displacement ellipsoid plot of \( [\text{FeCl}_3\text{Pr}] [\text{FeCl}_4^-] \) (7) (50 % probability ellipsoids) (CCDC 1579210). Hydrogen atoms and the \( \text{FeCl}_4^- \) counterion have been omitted for clarity. The crystal of \( [\text{FeCl}_3\text{Pr}] [\text{FeCl}_4^-] \) reveals the presence of two independent \( [\text{FeCl}_3\text{Pr}]^+ \) cations and two independent \( [\text{FeCl}_4^-]^- \) anions in the asymmetric unit.

\[ \text{Fe}(\text{Cl})\text{L}_3\text{Pr}[\text{FeCl}_4^-] \text{ (7) crystallizes as two independent molecules (next to the tetrachlorido ferrate) with almost identical bond angles and distances. They both have a trigonal bipyramidal geometry (} t_{5\#1} = 0.95 \text{ and } t_{5\#2} = 0.98 \text{ (Table 1))} \text{. The } P_1–\text{Fe}_1, P_2–\text{Fe}_1 \text{ and } P_3–\text{Fe}_1 \text{ bond lengths are elongated compared to the } [\text{FeCl}(\text{L}_1\text{H})]^+ \text{ unit, which is likely a result of the more electron-donating diisopropylphosphine groups. The other angles and distances are comparable to the } [\text{FeCl}(\text{L}_1\text{H})]^+ \text{ unit and values reported in literature} \text{.} \]

The presence of tetrachlorido ferrates as counterions is undesirable as iron chlorides could interfere during the follow-up redox chemistry. Therefore, a method previously described by Beller was used\(^{[11]} \) that involved the coordination of \( \text{L}^1\text{H} \) to \( \text{Fe(BF}_4)_2 \) (Figure 8).

Stirring of stoichiometric amounts of \( \text{L}^1\text{H} \) and \( \text{Fe(BF}_4)_2 \) in 1:1 (v/v) THF/toluene mixture at 70 °C for three days led to precipi-
tation of a purple powder in significant amounts. Full conversion was, however, not reached as indicated by the presence of free ligand in the $^3P$ NMR spectrum of the supernatant. The exact structure of this highly oxygen sensitive purple solid could not be determined due to its paramagnetism and poor solubility in $\text{D}_8$THF. However, dissolution of the purple solid in acetonitrile caused an immediate color change from purple to orange. This orange solution was diagnostically as evidenced by $^3P$ NMR spectroscopy, which indicates that the coordination environment around the metal center has changed. The $^3P$ NMR spectrum shows a similar splitting pattern as previously reported for the octahedral Ru(Cl)$_2$L$_1^{\text{MeCN}}$ complex.$^{[23]}$ The integral-ratio of $1$ ($\delta = 116.77$ ppm, $dt$); $2$ ($\delta = 97.59$ ppm, $t$); $1$ ($\delta = 56.18$ ppm, $dt$) confirms formation of an octahedral geometry around the metal center. 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 features two independent $\text{[FeL}^{2+}]^{2+}$ units, which indeed show both an octahedral geometry around the metal center of the $\text{[Fe(MeCN)]L}^{1+}\text{(BF}_4\text{)}_2$ complex 8 (Figure 9). The two cis sites in this complex are occupied by two acetonitrile ligands. The P1–Fe1–P2 [163.17(3)$^\circ$], P3–Fe1–N4 [177.49(7)$^\circ$], and the P4–Fe1–N5 angle [175.49(7)$^\circ$] 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$_{\text{eq}}$–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.

Reduction of $\text{[Co(Cl)L}^{1+}]^2\text{BF}_4$

In order to gain insight in the reduction potentials needed for the cobalt complexes to form the hypothetical Co$^0$L$_1^{1+}$N$_2$ complex, the $\text{[Co(Cl)L}^{1+}]^2\text{BF}_4$ (1b) complex was analyzed electrochemically. The CV of this cobalt complex shows one reversible redox couple ($E^{1/2}_{\text{F}} = –0.56$ V vs. Fc/Fc$^+$), below which Co$^0$ complex $\text{[Co(Cl)L}^{1+}]^2\text{BF}_4$ is reduced to Co$^+$ complex $\text{[Co(Cl)L}^{1+}]$ (see the Supporting Information). This value is slightly more negative than for the reversible Rh$^0$/Rh$^+$ couple of the rhodium [Rh(Cl)L$^{1+}$]PF$_6$ analogue ($E^{1/2}_{\text{F}} = –0.4$ V vs. Fc/Fc$^+$),$^{[20]}$ and comparable to the reversible Co$^0$/Co$^+$ couple of the [Co(PPh$_3$)$_3$(CH$_3$CN)]BF$_4$ complex ($E^{1/2}_{\text{F}} = –0.54$ V).$^{[48]}$ 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$^+$ to Co$^0$, which could lead to binding of the dinitrogen to the cobalt center. Consequently, we also tried to reduce the $\text{[Co(Cl)L}^{1+}]^2\text{BF}_4$ (1b) complex chemically. The chemical reduction of the $\text{[Co(Cl)L}^{1+}]^2\text{BF}_4$ 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. In addition, in situ analysis of the reaction mixture by $^3P$ NMR spectroscopy showed signals indicative of ligand decomposition. Ligand decomposition may be responsible for the second reduction peak observed in the CV ($E = –2.4$ 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 $\text{[Ni(Cl)L}^{1+}]^2\text{BF}_4$

We also investigated the reduction potentials of the nickel complex using electrolysis (see the Supporting Information).
Similar as for the cobalt analogue, the CV of 2b shows one reversible reduction-oxidation peak at $E^{1/2} = -1.0$ V vs. Fe/Fe$^\circ$ V. In addition, two non-reversible reduction peaks were observed ($E = -2.0$ V vs. Fe/Fe$^\circ$ and $E = -2.5$ V vs. Fe/Fe$^\circ$). CV measurements of [Ni(PP)$_3$(CH$_2$CN)](BF$_4$)$_2$ showed only one reversible redox couple ($E^{1/2} = -1.03$ V vs. Fe/Fe$^\circ$; likely the Ni$^{II}$/Ni$^I$ couple) and one non-reversible reduction peak, ($E^{0} = -1.28$ V vs. Fe/Fe$^\circ$; likely the Ni$^I$/Ni$^0$ couple). The chemical reduction of our [NiL$^1$H]$^1$BF$_4$ (2b) complex with two equivalents of KC$_8$ resulted in formation of a yellow precipitate. 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 any IR signal corresponding to an N$_2$ ligand bound to nickel. Comparable to the cobalt analogue, this result likely indicates that the ligand does not facilitate dinitrogen coordination when bound to nickel(0).

Reduction of [Fe(Cl)L$^1$H]$^1$BF$_4$

Next, we investigated whether it was possible to reduce the [Fe(Cl)L$^1$H]$^1$BF$_4$ (3) complex electrochemically. The cyclic voltammogram (see Figure S19) of [Fe(Cl)L$^1$H]$^1$BF$_4$ (3) in THF shows two reversible redox couples, one at $E^{1/2} = -0.96$ V vs. Ag/AgCl and one at $E^{1/2} = -1.29$ V vs. Ag/AgCl, corresponding to the Fe$^{II}$/Fe$^I$ and Fe$^I$/Fe$^0$ couple respectively. The reduction potential is much lower than the earlier mentioned paramagnetic [Fe(Cl)L$^1$H]$^1$ complex of Bianchini ($E^{1/2} = -0.64$ V vs. Ag/AgCl). Like Bianchini’s complex, the reduction of Fe$^0$ to Fe$^I$ 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 [Fe(Cl)L$^1$H]$^1$BF$_4$ (3) complex chemically and bind dinitrogen to the metal center. However, the addition of two equivalents of KC$_8$ in the presence of N$_2$ led to the formation of the Fe(N$_2$)L$^1$H (9) complex as indicated by the N$_2$ stretch frequency observed in the IR spectrum (Figure 10 and Table 3). Encouraged by this result we also attempted to reduce the other iron complexes with KC$_8$.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E^{0}$ $^1$M$/M^0$</th>
<th>$E^{0}$ $^2$M$/M^1$</th>
</tr>
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<tbody>
<tr>
<td>[Co(Cl)L$^1$H]$^1$BF$_4$ (1b)</td>
<td>$-0.56$ V</td>
<td>$-0.96$ V</td>
</tr>
<tr>
<td>[Ni(Cl)L$^1$H]$^1$BF$_4$ (2b)</td>
<td>$-1.00$ V</td>
<td>$-1.90$ V</td>
</tr>
<tr>
<td>[Fe(Cl)L$^1$H]$^1$BF$_4$ (3)</td>
<td>$-0.38$ V</td>
<td>$-1.90$ V</td>
</tr>
</tbody>
</table>

Reduction of Other Iron(+II)ClPP$_3$ Complexes

The in situ formed iron(0)N$_2$PP$_3$ complexes, prepared by two-electron reduction of the corresponding iron(+II) complexes with KC$_8$, all showed coordination of dinitrogen to the iron metal center as indicated by infrared spectroscopy measurements (Table 4). The Fe(N$_2$)L$^2$H complex 12 has the highest IR stretch frequency ($\nu_{N_2} = 2018$ cm$^{-1}$) and Fe(N$_2$)L$^3$Pr$^-$ (13) has the lowest IR stretch frequency ($\nu_{N_2} = 2081$ cm$^{-1}$) in the infrared spectrum.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_{N_2}$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(N$_2$)L$^1$H (9)</td>
<td>2018</td>
</tr>
<tr>
<td>Fe(N$_2$)L$^1$Fe$^{III}$ (10)</td>
<td>2051</td>
</tr>
<tr>
<td>Fe(N$_2$)L$^1$OMe$^-$ (11)</td>
<td>2068</td>
</tr>
<tr>
<td>Fe(N$_2$)L$^2$H (12)</td>
<td>2081</td>
</tr>
<tr>
<td>Fe(N$_2$)L$^3$Pr$^-$ (13)</td>
<td>2081</td>
</tr>
</tbody>
</table>

As expected, the extent of activation of N$_2$ by iron complexes with the 3-methylindole based tetraphosphine ligands L$^1$H, L$^1$CF$_3$, L$^1$OMe and L$^2$H is higher than for the analogous rhenium complexes. The increase of the electron donating capacity of the substituents of the equatorially coordinated phosphines when going from L$^1$CF$_3$ to L$^3$Pr$^-$ results in a clear shift of the N$_2$ stretch frequency to lower wavenumbers. The weakest activation of the N$_2$ ligand is observed in the case of the connectivity isomer L$^2$, which features a more $\pi$-acidic pivotal phosphine (trans to the N$_2$). This is in line with the studies of the influence of $\pi$-acidity of the donors trans to molybdenum-coordinated N$_2$ by Tucek et al. who reported that when going from purely $\sigma$-donating N-donor to a slightly $\pi$-acidic P-donor the N$_2$ stretch frequency shifts to higher wavenumbers. The effect of the trans-effect of nitrogen vs. phosphorus in terms of N$_2$ activation is also apparent when comparing the IR data for Fe$^0$(N$_2$)[N(CH$_3$CH$_2$PPh$_2$)$_2$]$_2$, $\nu_{N_2} = 1967$ cm$^{-1}$ vs. Fe$^0$(N$_2$)[P(CH$_3$CH$_2$PPh$_2$)$_2$]$_2$, $\nu_{N_2} = 1985$ cm$^{-1}$ as reported by the groups of George and Zubieta and Field, respectively.
Compared to the iron complexes with tripodal tetradeutate ligands used by the group of Peters for N2 reduction to ammonia or hydrazine,[51–53] the dinitrogen complexes reported in this work reveal higher stretch frequencies of the N2 ligand. For instance, the dinitrogen complexes of iron(0) with ligands featuring three diisopropyl phosphine donors connected via a phenylene linker to the pivotal B, C– and Si– coordination centers Fe0(BP<sub>i</sub>Pr<sub>3</sub>N<sub>2</sub>)[52], [Fe0(CP<sub>i</sub>Pr<sub>3</sub>)N<sub>2</sub>][53], [Fe0(SiP<sub>i</sub>Pr<sub>3</sub>)N<sub>2</sub>]–[52] reveal ν<sub>N2</sub> = 2011 cm<sup>–1</sup>, 1870 cm<sup>–1</sup> and 1891 cm<sup>–1</sup> respectively. Since ligands CP<sub>i</sub>Pr<sub>3</sub> and SiP<sub>i</sub>Pr<sub>3</sub> are anionic, the extent of π-back donation to the N2 moiety in their respective iron complexes is obviously higher than in the case of the L<sub>3</sub>iPr complex. However, the overall donating capability of BP<sub>i</sub>Pr<sub>3</sub> (which is the most effective tripodal system for N2 activation[15]) to iron is similar to L<sub>3</sub>iPr. The major difference between BP<sub>i</sub>Pr<sub>3</sub> and the 3-methylindolyl-based ligand systems presented in this work is the capability of BP<sub>i</sub>Pr<sub>3</sub> to accommodate a negatively charged [Fe–I(N<sub>2</sub>)L]<– complex upon one electron reduction of the neutral Fe(N<sub>2</sub>)L, resulting in further weakening of the N–N bond (ν<sub>N2</sub> = 1905 cm<sup>–1</sup>), and rendering this complex an active catalyst for ammonia formation. The stabilization of such Fe<sup>1</sup> species is possible thanks to the incorporation of the σ-acidic boron atom in the BP<sub>i</sub>Pr<sub>3</sub> ligand. Unfortunately, the addition of one extra equivalent of KC8 to Fe0(N<sub>2</sub>)PP<sub>3</sub> led to the detection of decomposed ligand in the 31P NMR spectra. In addition, no new bands corresponding to the N2 stretch frequency were detected in the infrared spectrum. The resulting reaction mixtures proved to be EPR silent. This led us to conclude that such putative negatively charged complexes are too unstable to be detected, or perhaps not formed at all.

All of the reaction mixtures that were prepared for the in situ analysis of the N2 stretch frequency with infrared spectroscopy were set for crystallization by slow diffusion evaporation with pentane. In the case of Fe(Cl)L<sub>1</sub>H (14), Fe(Cl)L<sub>2</sub>H (15) and Fe(Cl)L<sub>3</sub>iPr (16), crystals suitable for X-ray diffraction were obtained for some of these batches (Figure 11). In all three cases, analysis of the crystal structure showed the presence of the Fe(Cl)L complex, indicating that the reduction reactions intended to form FeN<sub>2</sub>L did not go to completion, and besides the desired iron(0) species also iron(+I) complexes are formed. As expected for a d<sup>7</sup> metal complexes, all three iron(+I) complexes feature a distorted trigonal bipyramidal geometry around the metal center due to the Jahn–Teller effect: Fe(Cl)L<sub>1</sub>H (τ<sub>s</sub> = 0.75), Fe(Cl)L<sub>2</sub>H (τ<sub>s</sub> = 0.69) and Fe(Cl)L<sub>3</sub>iPr (τ<sub>s</sub> = 0.75) (Table 5).

Upon addition of a slight excess of KC8 to the [Fe(Cl)L<sub>1</sub>H]<BF<sub>4</sub> complex, a more intense absorption of the N2 moiety was observed in the IR spectrum. When this red reaction mixture was set for crystallization by layering with pentane, crystals of Fe(N<sub>2</sub>)L<sub>1</sub>H (9) complex formed that were suitable for X-ray diffraction analysis (Figure 12). The crystal structure of Fe(N<sub>2</sub>)L<sub>1</sub>H reveals a nearly ideal trigonal bipyramidal geometry around the metal center (τ<sub>s</sub> = 0.95)[41] The structure is more symmetrical than the iron(+II) and ruthenium(0)[23] analogues, but structurally comparable to the known Fe(N<sub>2</sub>)(PP<sub>i</sub>Pr<sub>3</sub>) (ν<sub>N2</sub> = 1985 cm<sup>–1</sup>) complex.[19] The N–N bond length of FeN<sub>2</sub>L<sub>1</sub>H is slightly shorter [1.118(5) Å] than in FeN<sub>2</sub>(PP<sub>i</sub>Pr<sub>3</sub>) [1.1279(16) Å], which is in concordance with a less activated N<sub>2</sub> moiety in Fe(N<sub>2</sub>)L<sub>1</sub>H. These experiments therefore show that electronic variation in the ligands that coordinate to the iron metal have a clear effect on the activation of N<sub>2</sub> bound to Fe.
In conclusion, we have shown that the coordination of iron(II), cobalt(+II) and nickel(+II) to several tripodal 3-methylindole phosphine based ligands results in the formation of the corresponding cationic metal(II) complexes. All of the complexes featuring the bulky chlorido ligand are five coordinate, with a bipyramidal geometry, where the cobalt complex is the most distorted as a result of the Jahn–Teller effect. The geometry of the nickel complex is more distorted than that of iron, which is distorted as a result of the smaller atomic radius of the nickel atom. The 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: The complex Fe(N2)L2+ featuring the most π-acidic phosphorus donor trans to the coordinated N2 ligand has the highest IR stretch frequency (νN2 = 2068 cm⁻¹) while introduction of strongly s-donating groups in complex Fe(N2)L3⁺ resulted in the lowest IR stretch frequency (νN2 = 2018 cm⁻¹) within the Fe(N2)L series. The coordination of dinitrogen to the iron(0)PP3 complexes is interesting in the light of the potential application of these complexes as dinitrogen reduction catalysts, as the coordination of dinitrogen to the metal is the first step in dinitrogen reduction to ammonia.

### 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 performed with a Bruker DRX 300, Bruker AV 400, Bruker DRX 500, 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. LC/MS analysis was performed with an Agilent 1200 Series HPLC operated with Agilent 6410 QQQ triple quadrupole tandem mass spectrometer. X-ray diffraction data were collected on a Bruker Smart Apex II diffractometer using Mo Kα radiation. The intensities were integrated with the SAINT software suite.

**Structure Solution and Refinement:** All structures were solved using SHELXT and refined against F² with SHELXL-2013. The structures were solved with the SHELXT program using the MultiScan absorption correction technique and scaled with SADABS. The structures were solved using the SHELXT program with the Multi-Scan absorption correction technique and scaled with SADABS. The structures were solved using the SHELXT program with the Multi-Scan absorption correction technique and scaled with SADABS.
[FeCl₃] have solvent accessible voids filled with disordered solvent that could not be satisfactorily refined. Their contribution to the structure factors in the refinement was taken into account with the PLATON/SQUEEZE approach.\(^{[19]}\)

**Tris-2-(3-methyl-N-diisoproplyphosphinoindoly)phosphine (L₃\(^{2+}\)):** Tris-2-(3-methylindolyl)phosphine (1.02 g; 2.42 mmol; 1.0 equiv.) was dissolved in THF (50 mL) and cooled to -78 °C. This was added nBuLi (2.5 M in hexanes; 2.9 mL; 7.38 mmol; 3.0 equiv.) dropwise and stirred for 1 h resulting in a yellow solution. Subsequently, chlorodisoproplyphosphine (1.2 mL; 7.38 mmol; 3.0 equiv.) was added dropwise and the mixture was stirred for 3 d allowing the reaction mixture to warm to room temperature. The yellow solution was evaporated to dryness, and the thus formed solid was extracted with CH₂Cl₂ (3 × 10 mL). The combined CH₂Cl₂ solutions were filtered through basic alumina and evaporated in vacuo. The formed solid was washed with Et₂O (3 × 1 mL), yielding the product in pure form as a white powder (0.83 g; 45 % yield).

\(^{1}H\)(\(^{31}P\)) NMR (300 MHz, CDCl₃): \(\delta = 7.51\) (d, \(J = 16.4\) Hz, 3 H), 7.49 (d, \(J = 15.8\) Hz, 3 H), 7.21 (m, 6 H), 2.93–2.61 (m, 6 H), 1.90 (s, 9 H), 1.24 (d, \(J = 6.9\) Hz, 9 H), 1.11 (d, \(J = 7.0\) Hz, 9 H), 0.88 (d, \(J = 6.8\) Hz, 9 H), 0.46 (d, \(J = 6.9\) Hz, 9 H) ppm. \(^{31}P\) NMR (121 MHz, CDCl₃): \(\delta = 63.35\) (d, \(J = 168.7\) Hz, 3 P), -77.94 (q, \(J = 168.8\) Hz, 1 P) ppm.

**NiCl\(_2\)(BF₄) \(\cdot\) (bf) \(\cdot\) (7):** Compound L\(^{3+}\) \(\cdot\) (23.1 mg; 0.097 mmol; 1.0 equiv.) was suspended in THF (10 mL) and stirred overnight. The green precipitate was filtered off, washed with Et₂O and was dried in vacuo yielding the complex as a green solid. Yield: 98.9 mg (0.086 mmol, 87.9 %); \(^{1}H\) NMR (300 MHz, CDCl₃): \(\delta = 7.81\) (d, \(J = 8.1\) Hz, 3 H), 7.27–7.17 (m, 9 H), 7.12–6.82 (m, 29 H), 6.29 (d, \(J = 8.5\) Hz, 3 H), 2.67 (s, 9 H) ppm. \(^{31}P\) NMR (121 MHz, CDCl₃): \(\delta = 61.06\) (d, \(J = 47.1\) Hz, 3 P), 25.91 (q, \(J = 47.4\) Hz, 1 P) ppm. Slow diffusion evaporation of hexane to a dichloromethane solution of NiCl\(_2\)(BF₄) resulted in the formation of crystals suitable for X-ray diffraction analysis. Mass Analysis (CS-ESI) [NiCl\(_{4}\)(BF₄)\(_2\)]: found: 1066.2097 calcd.: 1066.2075; negative: no fragments belonging to the complex could be observed. The NMR spectra of this complex are identical to [NiCl\(_{4}\)(BF₄)\(_2\)].

**Fe(Cl)L\(_1\)H \(\cdot\) (BF₄) \(\cdot\) (1b):** Compound L\(^{3+}\) \(\cdot\) (104.1 mg; 0.11 mmol; 1.0 equiv.), NaBF₄ (113 mg; 0.12 mmol; 1.0 equiv.) and FeCl₂ (0.178 g; 1.36 mmol; 2.1 equiv.) were suspended in THF (10 mL) and stirred overnight. The brown precipitate was filtered off, washed with pentane and dried in vacuo yielding the complex as a brown 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 FeCl\(_2\)(BF₄) with pentane. \(^{1}H\) NMR (300 MHz, CDCl₃): \(\delta = 17.51\) (d, \(J = 16.4\) Hz, 3 H), 7.49 (d, \(J = 15.8\) Hz, 3 H), 7.21 (m, 6 H), 2.93–2.61 (m, 6 H), 1.90 (s, 9 H), 1.24 (d, \(J = 6.9\) Hz, 9 H), 1.11 (d, \(J = 7.0\) Hz, 9 H), 0.88 (d, \(J = 6.8\) Hz, 9 H), 0.46 (d, \(J = 6.9\) Hz, 9 H) ppm.

**NiCl\(_{4}\)(BF₄) \(\cdot\) (bf) \(\cdot\) (7):** Compound L\(^{3+}\) \(\cdot\) (23.1 mg; 0.097 mmol; 1.0 equiv.) was suspended in THF (10 mL) and stirred overnight. The green precipitate was filtered off, washed with Et₂O and was dried in vacuo yielding the complex as a green solid. Yield: 98.9 mg (0.086 mmol, 87.9 %); \(^{1}H\) NMR (300 MHz, CDCl₃): \(\delta = 7.81\) (d, \(J = 8.1\) Hz, 3 H), 7.27–7.17 (m, 9 H), 7.12–6.82 (m, 29 H), 6.29 (d, \(J = 8.5\) Hz, 3 H), 2.67 (s, 9 H) ppm. \(^{31}P\) NMR (121 MHz, CDCl₃): \(\delta = 61.06\) (d, \(J = 47.1\) Hz, 3 P), 25.91 (q, \(J = 47.4\) Hz, 1 P) ppm. Slow diffusion evaporation of hexane to a dichloromethane solution of NiCl\(_2\)(BF₄) resulted in the formation of crystals suitable for X-ray diffraction analysis. Mass Analysis (CS-ESI) [NiCl\(_{4}\)(BF₄)\(_2\)]: found: 1066.2097 calcd.: 1066.2075; negative: no fragments belonging to the complex could be observed. The NMR spectra of this complex are identical to [NiCl\(_{4}\)(BF₄)\(_2\)].
[Fe(MeCN)₅L₁H][BF₄]₂ (8): 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. ¹H NMR (300 MHz, CD₃CN): 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. ¹³C NMR (121 MHz, CD₂CN): δ = 116.77 (q), 97.59 (t, J = 44.2 Hz), 56.18 (q) ppm. The ¹H- and ¹³C-NMR spectrum could not be obtained in pure form. ¹⁹F NMR (282 MHz, CD₃CN): δ = 115.10 ppm. Mass analysis (CSI) [FeL¹⁺H⁺]⁺: found: 514.6169, calcld.: 514.6192; [FeL¹⁺]²⁻: found: 1048.2362 calculated: 1048.2369; BF₄⁻: found: 87.0049, calcld.: 87.0029.

Standard Procedure for the Reduction of the Complexes with KC₈: 20 mg of the complex was suspended with 2–5 equiv. of KC₈ in 2 mL of THF in the glovebox and stirred for 2–3 h. 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 FeClL¹H⁺ (14), FeCl₂L²H⁺ (15), FeCl₃L³H⁺ (16) and FeN₂L¹H⁺ (9). Crystals of FeN₂L¹H⁺ (9) were obtained by layering of the THF solution with pentane. CCDC 1579207 (for 1a), 1579208 (for 2a), 1579209 (for 3b), 1579210 (for 7), 1579211 (for 8), 1579212 (for 14), 1579213 (for 15), 1579214 (for 16), and 1579215 (for 9) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgments

We thank the National Research School Combination Catalysis (NRSC-C) and the Netherlands Organization for Scientific Research (NWO-CW) for a VENI grant 722.013.002 to W. I. D., and the University of Amsterdam (RAP Sustainable Chemistry) for funding. We thank Jan Meine Ernsting for assistance with NMR spectroscopy and Ed Zuidinga for mass spectrometry measurements.

Keywords: iron · cobalt · nickel · dinitrogen complexes · P ligands


Received: October 16, 2017