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 Fe⁰N₂L¹H 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, tetradeutate 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, tetradeutate 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 Rh²⁺[20] and Ru²⁺ 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 tetradeutate phosphine based complexes using either PPPh₃ = P(CH₂CH₂PPh₂)₃ or PPiPr₃ = [P(CH₂CH₂P(iPr)₂)₃] coordinated to iron(II), cobalt(II) and nickel(II) have been exten-

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Figure 1. Coordination of cobalt(II) and nickel(II) chlorides to ligand L¹H forming the corresponding cobalt(II) and nickel(II) complexes 1 and 2.
sively studied.\textsuperscript{[25–30]} 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.\textsuperscript{[29,31]} 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.

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-diphenylphosphonyl)-3-methyl-1H-indol-2-yl)phosphane (L¹H) 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 d⁶ to d⁷ to d⁸ by going from iron(⁺II) to cobalt(⁺II) to nickel(⁺II). Additionally, coordination studies of a variety of 3-methylindole based ligands (L²H, L³H and L³PPH) 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 N₂ upon two-electron reduction with KC₈. In addition, we explored whether ligand modification leads to observable electronic effects in the N≡N stretch frequency when the PP₃ 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 L¹H, L²H and L³PPH and iron(⁰) with ligand L¹H.

**Results and Discussion**

**Formation of Mono and Binary Cobalt L¹H Complexes**

We started our investigations with coordination studies of the tripodal indolyl-based tetraphosphine ligand (L¹H) to cobalt(⁺II). Stoichiometric amounts of L¹H and CoCl₂·6H₂O in THF did not lead to full consumption of L¹H as judged by in situ \(^{31}\)P NMR spectroscopy. Cold Spray Electron Ionization Mass Spectroscopy (CS-ESI-MS) revealed the presence of CoCl₄⁻ dianion which pointed to the possibility of the formation of a pentacoordinate [CoClL¹H]₂[CoCl₄] (1a) complex in which a part of the CoCl₄ 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 L¹H with CoCl₂ in a 2:3 stoichiometry to quantitatively form the binary [CoClL¹H]₂[CoCl₄] complex 1a. The monometallic complex could be obtained when the reaction was carried out in the presence of NaBF₄ (Figure 1) with the sodium cation acting as the scavenger of one of the chloride anions. This led to clean formation of [CoL¹H]BF₄ (1b) from stoichiometric amounts of L¹H and CoCl₂·6H₂O in THF.

CS-ESI mass spectroscopy analysis showed the presence of the [Co(Cl)L¹H]⁺ cation in both [Co(Cl)L¹H]BF₄ (1b) and [Co(Cl)L¹H₂][CoCl₄] (1a) samples (see experimental section). Similar to findings reported by Braunstein and co-workers the [Co(Cl)L¹H₂][CoCl₄] fragment could be detected in the [Co(Cl)L¹H₂][CoCl₄] sample, indicating formation of the proposed binary complex.\textsuperscript{[29,40]} Both the cationic and anionic cobalt complexes are paramagnetic. EPR analysis of the [CoL¹H]BF₄ (1b) and [Co(Cl)L¹H₂][CoCl₄] (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(Cl)L¹H₂][CoCl₄] shows an extra signal (700–2500 G) corresponding to the high spin tetrachlorido cobaltate anion, which is absent in the [CoL¹H]BF₄.

Layering a dichloromethane solution of [Co(Cl)L¹H₂][CoCl₄] with pentane resulted in the formation of single crystals suitable for X-ray diffraction analysis (Figure 3). As expected, the binary complex [Co(Cl)L¹H₂][CoCl₄] 1a is present in the crystal structure. The two [Co(Cl)L¹H⁺]⁺ 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 (\(r_{567} = 0.55\) and \(r_{572} = 0.67\))\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 [RhClL¹H]PF₆ (\(r_{57} = 0.55\)).\textsuperscript{[20]} The four strong-field phosphine ligands favor the formation of low spin complexes, thus, d⁷ 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 d⁶ or low spin d⁸ 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]2[CoCl4] (1a) and [Ni(Cl)L1H]2[NiCl4] (2a) complexes.

<table>
<thead>
<tr>
<th></th>
<th>[Co(Cl)L1H]2[CoCl4] (1a)</th>
<th>[Ni(Cl)L1H]2[NiCl4] (2a)</th>
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</thead>
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<td></td>
<td>[Co(Cl)L1H]+ #1</td>
<td>[Ni(Cl)L1H]+ #1</td>
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<tr>
<td>M1–P1</td>
<td>2.242(11)</td>
<td>2.2187(10)</td>
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<td>M1–P2</td>
<td>2.259(11)</td>
<td>2.2435(10)</td>
</tr>
<tr>
<td>M1–P3</td>
<td>2.2673(11)</td>
<td>2.2308(10)</td>
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<td>M1–P4</td>
<td>2.1432(11)</td>
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<td>M1–Cl1</td>
<td>2.2401(11)</td>
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<td>116.25(4)</td>
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<td>P2–M1–P3</td>
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<td>111.39(4)</td>
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<tr>
<td>P1–M1–P4</td>
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<td>86.56(4)</td>
</tr>
<tr>
<td>P2–M1–P4</td>
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<td>86.30(4)</td>
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<td>Cl1–M1–P4</td>
<td>173.63(5)</td>
<td>173.23(4)</td>
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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]2[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 $^{31}$P NMR spectra of Ni(Cl)L1HBF4 (1b) and [Ni(Cl)L1H]2[NiCl4] (1a) show one doublet ($\delta = 61.06$ ppm) and one quartet ($\delta = 25.91$ ppm), indicating a $C_3$-symmetrical trigonal bipyramidal geometry in solution (on the NMR time scale). $C_3$-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][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]2[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...
[Ni(Cl)L1H]+ ion in both [Ni(Cl)L1H]BF4 (2b) and [Ni(Cl)L1H]2-
[NiCl4] (2a) (see experimental section). Slow diffusion of hexane
to a dichloromethane solution of [Ni(Cl)L1H]2[NiCl4] resulted in
the formation of crystals suitable for X-ray diffraction analysis
(Figure 4).

The crystal structure shows the presence of the binary
[Ni(Cl)L1H]2[NiCl4] complex 2a where the two [Ni(Cl)L1H]+ units
crystallize as two independent molecules. The [Ni(Cl)L1H]+ units
feature a distorted trigonal bipyramidal geometry around the
metal center (τ5#1 = 0.70 and τ5#2 = 0.86) (Table 1).141) The ge-
ometry is less distorted than the geometry of the cobalt ana-
logues (vide supra), but more distorted than the geometry of
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 of the independent
structures and 126.51(4)° for the other, which is still close to the
ideal 120° angle for the TBP geometry.

**Formation of Iron PP3 Complexes**

The above results show that the coordination of the tetra-
dentate indolyl phosphate ligand L1H to d6 nickel(II) and d7
coalt(II) chlorides results in formation of (highly distorted in
the case of cobalt) trigonal bipyramidal complexes of the type
[MII(Cl)L1H]+ and that in the absence of non-coordinating BF4–
anion, binary tetrachloro metallocene complexes are formed. We
next turned our attention to iron, and the results of these inves-
tigations are described in the following section. Whereas in the
case of nickel and cobalt the L1H ligand complexes are penta-
coordinate, complexation of this ligand to d6 iron(II) could in
principle result in formation of a hexacoordinate 18 VE complex,
as was observed for iron’s heavier analogue ruthenium,122,244) or
alternatively in the formation of a pentacoordinate 16 VE com-
plex. 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 spec-
trometry analysis in both positive and negative modes shows
the presence of both the [Fe(Cl)L1H]+ complex and the BF4 counterion respectively, which is in accordance with a five-co-
dinate geometry around the metal center, supported by one non-coordinating anion. These data thus indicate that the syn-
thetized compound is a pentacoordinate iron complex
[Fe(Cl)L1H]BF4 (3b). DFT calculations suggest that the lowest energy state of the [Fe(Cl)L1H]+ cation is an intermediate spin,
paramagnetic trigonal bipyramidal complex443 (d5) iron(III) (d6)
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(Cl)L1H]BF4 (3b) with pentane.

As anticipated, the crystal structure shows a trigonal bi-
pyramidal geometry around the metal center (Figure 5). The
overall crystal structural data is in good agreement with other
tripodal five-coordinate tetraphosphone TBP iron(II) com-
exes.110,11,19,28,37,46) The longest equatorial angle P1–Fe1–P2 of
120.51(4)° (Table 2) fits well with that of an ideal TBP geometry,
which is in correspondence with a τ5 = 0.92.141)

Figure 5. Displacement ellipsoid plot of [Fe(Cl)L1H]BF4 (3b) (50 % probability ellipsoids) (CCDC 1579209). Dichloromethane solvent molecule and hydrogen
atoms and the BF4– counterion have been omitted for clarity.

Table 2. Selected bond lengths and angles of the [Fe(Cl)L1H]BF4 and
[Fe(Cl)L3H]+[FeCl4]2 complexes.

<table>
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<th>[Fe(Cl)L1H]+</th>
<th>[Fe(Cl)L3H]+[FeCl4]2</th>
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<tr>
<td>M1–P1</td>
<td>2.2721(9)</td>
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<td>M1–P2</td>
<td>2.2765(10)</td>
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<td>M1–P3</td>
<td>2.2748(9)</td>
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<td>M1–P4</td>
<td>2.1952(8)</td>
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<td>M1–P5</td>
<td>2.2145(8)</td>
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<td>P1–M1–P2</td>
<td>118.37(3)</td>
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<td>P2–M1–P3</td>
<td>117.52(4)</td>
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<td>P3–M1–P4</td>
<td>117.54(2)</td>
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<td>P4–M1–P5</td>
<td>83.36(3)</td>
</tr>
<tr>
<td>C11–M1–P4</td>
<td>178.58(4)</td>
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Subsequently, we explored the coordination of FeCl2 to the
PP3 ligands L1H, L1OMe, L2H, and L3H in the presence of
NaBF4 (Figure 6) to form complexes 4, 5, 6, and 7, respecti-
vely. The new ligand L3H was prepared by reacting the lithium salt
of tris-2-(3-methylindolyl)phosphine47 with disisopropyl chloro-
phosphine. Coordination of ligands other than L1H to iron in
presence of NaBF4 did not provide the monometallic complex
[Fe(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 spec-
trometry analysis of these reaction mixtures in the positive
mode shows the presence of the [Fe(Cl)L]+ cation, which indi-
cates that the ligand does coordinate to the iron center. Ana-
ly-
sis in the negative mode showed the presence of the expected BF₄⁻ anion but also the presence of the FeCl₃⁻ and FeCl₄⁻ 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 L₃Pr with FeCl₂ in the presence of NaBF₄ 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 [FeCl₄]⁻ (likely formed in situ by a reaction of [FeCl₄]²⁻ with traces of oxygen) as counterion, resulting in the binary [Fe(Cl)L₃Pr][FeCl₄] complex 7 (Figure 7).

![Figure 6. Synthesis of L₃Pr and coordination of L₁CF₃, L₁OMe, L₃Pr and L₂H to FeCl₂ in the presence of NaBF₄.](image)

Figure 6. Synthesis of L₃Pr and coordination of L₁CF₃, L₁OMe, L₃Pr and L₂H to FeCl₂ in the presence of NaBF₄.
tation of a purple powder in significant amounts. Full conversion was, however, not reached as indicated by the presence of free ligand in the $^{31}$P 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 D$_8$THF. 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 $^{31}$P NMR spectroscopy, which indicates that the coordination environment around the metal center has changed. The 31P NMR spectrum shows a similar splitting pattern as previously reported for the octahedral Ru(Cl)$_2$L$_1$H$^{14}$ 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 [FeL$_1$H$^{14}$]$^{2+}$ units, which indeed show both an octahedral geometry around the metal center of the [Fe(MeCN)$_2$L$_1$H$^{14}$](BF$_4$)$_2$ complex 8 (Figure 9). The two cis sites in this complex are occupied by two acetonitrile ligands. The P1–Fe1–P2 [163.17(3)°], P3–Fe1–N4 [177.49(7)°], and the P4–Fe1–N5 angle [175.49(7)°] are all close to the theoretical 180° 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.

Attempts to synthesize iron(+II) complexes with ligands L$_1$CF$_3$ and L$_1$OMe, provided 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.

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 their reduction in the presence of dinitrogen. In analogy to ruthenium,[23,24] the iron complexes may 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 formation of dinitrogen complexes upon reduction of these complexes is possible, we conducted cyclic voltammetry (CV) studies and in situ reduction of the new complexes in the presence of N$_2$.

Reduction of [Co(Cl)L$_1$H$^{14}$]BF$_4$

In order to gain insight in the reduction potentials needed for the cobalt complexes to form the hypothetical Co$^{0}$L$_1$H$^{14}$N$_2$ complex, the [Co(Cl)L$_1$H$^{14}$]BF$_4$ (1b) complex was analyzed electrochemically. The CV of this cobalt complex shows one reversible redox couple (\(E^{1/2} = -0.56\) V vs. Fc/Fc$^+$), below which Co$^{0}$ complex [Co(Cl)L$_1$H$^{14}$]BF$_4$ is reduced to Co$^+$ complex [Co(Cl)L$_1$H$^{14}$] (see the Supporting Information). This value is slightly more negative than for the reversible Rh$^0$/Rh$^+$ couple of the rhodium [Rh(Cl)L$_1$H$^{14}$]PF$_6$ analogue (\(E^{1/2} = -0.4\) V vs. Fc/Fc$^+$),[20] and comparable to the reversible Co$^0$/Co$^+$ couple of the [Co(PP$_{3}$Ph)$_2$(CH$_3$CN)]BF$_4$$_2$ complex (\(E^{1/2} = -0.54\) 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 [Co(Cl)L$_1$H$^{14}$]BF$_4$ (1b) complex chemically. The chemical reduction of the [Co(Cl)L$_1$H$^{14}$]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 $^{31}$P NMR spectroscopy showed signals indicative of ligand decomposition. Ligand decomposition may be responsible for the second reduction peak observed in the CV (\(E = -2.4\) 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 [Ni(Cl)L$_1$H$^{14}$]BF$_4$

We also investigated the reduction potentials of the nickel complex using electrochemistry (see the Supporting Information).
Reduction of [Fe(Cl)L1H]BF4

Next, we investigated whether it was possible to reduce the [Fe(Cl)L1H]BF4 complex electrochemically. The cyclic voltammogram (see Figure S19) of [Fe(Cl)L1H]BF4 in THF shows two reversible redox couples, one at $E_{1/2} = -0.38$ V vs. Ag/AgCl and one at $E_{1/2} = -1.29$ V vs. Ag/AgCl, corresponding to the FeIII/FeII and FeII/FeI couple respectively. The latter FeII/FeI reduction potential is much lower than the earlier mentioned paramagnetic [Fe(Cl)PPPh3]+ complex of Bianchini ($E_{1/2} = -0.64$ V vs. Ag/AgCl). Like Bianchini's complex, the reduction of FeI to Fe0 likely takes place very close to the reduction wave of THF, and can therefore not be determined. From this data it is not apparent if we would be able to reduce the [Fe(Cl)L1H]BF4 complex chemically and bind dinitrogen to the metal center. However, the addition of two equivalents of KC8 in the presence of N2 led to the formation of the Fe(N2)L1H (9) complex as indicated by the N2 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 KC8.

Reduction of Other Iron(+II)ClPP3 Complexes

The in situ formed iron(0)N2PP3 complexes, prepared by two-electron reduction of the corresponding iron(+II) complexes with KC8, all showed coordination of dinitrogen to the iron metal center as indicated by infrared spectroscopy measurements (Table 4). The Fe(N2)L2H complex 12 has the highest IR stretch frequency ($\nu_{N2} = 2068$ cm$^{-1}$) and Fe(N2)L3PP1 (13) has the lowest IR stretch frequency ($\nu_{N2} = 2018$ cm$^{-1}$) in the infrared spectrum.

As expected, the extent of activation of N2 by iron complexes with the 3-methylindole based tetraphosphine ligands L1H, L1CF3, L1OMe and L2H 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 L1CF3 to L3PP1 results in a clear shift of the N2 stretch frequency to lower wavenumbers. The weakest activation of the N2 ligand is observed in the case of the connectivity isomer L2, which features a more π-acidic pivotal phosphine (trans to the N2). This is in line with the studies of the influence of π-acidity of the donors trans to molybdenum-coordinated N2 by Tuczek et al. who reported that when going from purely σ-donating N-donor to a slightly π-acidic P-donor the N2 stretch frequency shifts to higher wavenumbers. The effect of the trans-effect of nitrogen vs. phosphorus in terms of N2 activation is also apparent when comparing the IR data for Fe(N2)L1(P(CH2CH2PPh2)3) ($\nu_{N2} = 1967$ cm$^{-1}$) vs. Fe(N2)L1b(P(CH2CH2PPh2)3) ($\nu_{N2} = 1985$ cm$^{-1}$) as reported by the groups of George and Zubieta and Field, respectively.

![Figure 10. Two-electron reduction of iron(II) complexes with 3-methylindole-based tripodal tetraphosphine ligands in the presence of N2.](image-url)
Compared to the iron complexes with tripodal tetradeutate ligands used by the group of Peters for N\textsubscript{2} reduction to ammonia or hydrazine\textsuperscript{[51–53]}, the dinitrogen complexes reported in this work reveal higher stretch frequencies of the N\textsubscript{2} 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 \textit{Fe}\textsubscript{0}(BP\textsubscript{i}Pr\textsubscript{3})N\textsubscript{2}\textsuperscript{[52]}, \textit{[Fe}\textsubscript{0}(CP\textsubscript{i}Pr\textsubscript{3})N\textsubscript{2}]\textsuperscript{–}\textsuperscript{[53]}, \textit{[Fe}\textsubscript{0}(SiP\textsubscript{i}Pr\textsubscript{3})N\textsubscript{2}]\textsuperscript{–}\textsuperscript{[52]} reveal \(\nu_{N\textsubscript{2}} = 2011\text{ cm}^{-1}\), 1870 \text{ cm}^{-1} and 1891 \text{ cm}^{-1} respectively. Since ligands CP\textsubscript{i}Pr\textsubscript{3} and SiP\textsubscript{i}Pr\textsubscript{3} are anionic, the extent of \(\pi\)-back donation to the N\textsubscript{2} moiety in their respective iron complexes is obviously higher than in the case of the \textit{L}\textsubscript{3}iPr complex. However, the overall donating capability of BP\textsubscript{i}Pr\textsubscript{3} (which is the most effective tripodal system for N\textsubscript{2} activation\textsuperscript{[15]}) to iron is similar to \textit{L}\textsubscript{3}iPr. The major difference between BP\textsubscript{i}Pr\textsubscript{3} and the 3-methylindolyl-based ligand systems presented in this work is the capability of BP\textsubscript{i}Pr\textsubscript{3} to accommodate a negatively charged [Fe\textsuperscript{−}(N\textsubscript{2}L)]\textsuperscript{–} complex upon one electron reduction of the neutral Fe(N\textsubscript{2}L), resulting in further weakening of the N–N bond (\(\nu_{N\textsubscript{2}} = 1905\text{ cm}^{-1}\)), and rendering this complex an active catalyst for ammonia formation. The stabilization of such Fe\textsuperscript{−} species is possible thanks to the incorporation of the \(\sigma\)-acidic boron atom in the BP\textsubscript{i}Pr\textsubscript{3} ligand. Unfortunately, the addition of one extra equivalent of KC\textsubscript{8} to Fe\textsubscript{0}(N\textsubscript{2}PP\textsubscript{3}) led to the detection of decomposed ligand in the \textsuperscript{31}P NMR spectra. In addition, no new bands corresponding to the N\textsubscript{2} 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 N\textsubscript{2} stretch frequency with infrared spectroscopy were set for crystallization by slow diffusion evaporation with pentane. In the case of Fe(Cl)L\textsubscript{1}H\textsuperscript{14}, Fe(Cl)L\textsubscript{2}H\textsuperscript{15} and Fe(Cl)L\textsubscript{3}Pr\textsuperscript{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 Fe\textsubscript{0}N\textsubscript{2}L did not go to completion, and besides the desired iron(0) species also iron(+I) complexes are formed. As expected for a d\textsuperscript{7} 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\textsubscript{1}H (\(r_{5} = 0.75\)), Fe(Cl)L\textsubscript{2}H (\(r_{5} = 0.69\)) and Fe(Cl)L\textsubscript{3}Pr (\(r_{5} = 0.75\)) (Table 5).

Upon addition of a slight excess of KC\textsubscript{8} to the [Fe(Cl)L\textsubscript{1}H]BF\textsubscript{4} complex, a more intense absorption of the N\textsubscript{2} moiety was observed in the IR spectrum. When this red reaction mixture was set for crystallization by layering with pentane, crystals of Fe\textsubscript{0}(N\textsubscript{2}L\textsubscript{1}H) (9) complex formed that were suitable for X-ray diffraction analysis (Figure 12). The crystal structure of Fe\textsubscript{0}(N\textsubscript{2}L\textsubscript{1}H) reveals a nearly ideal trigonal bipyramidal geometry around the metal center (\(r_{5} = 0.95\))\textsuperscript{[41]} The structure is more symmetrical than the iron(+II) and ruthenium(0)\textsuperscript{[23]} analogues, but structurally comparable to the known Fe\textsubscript{0}(N\textsubscript{2}PP\textsubscript{3}) (\(\nu_{N\textsubscript{2}} = 1985\text{ cm}^{-1}\)) complex\textsuperscript{[19]} The N–N bond length of Fe\textsubscript{0}(N\textsubscript{2}L\textsubscript{1}H) is slightly shorter [1.118(5) \text{ Å}] than in Fe\textsubscript{0}(PP\textsubscript{3}) [1.1279(16) \text{ Å}], which is in accordance with a less activated N\textsubscript{2} moiety in Fe(N\textsubscript{2}PP\textsubscript{3})\textsubscript{14}. 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\textsubscript{2} bound to Fe.
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 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 (distorted) trigonal bipyramidal 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 the Jahn–Teller effect.

The geometry of the nickel complex is more distorted than that of iron, which is likely a result of the smaller atomic radius of the nickel atom. The two-electron reduction of the nickel complex is more distorted than that of iron, which is distorted as a result of the Jahn–Teller effect. The geometry of the cobalt complex is the most distorted as a result of the Jahn–Teller effect.

In conclusion, we have shown that the coordination of iron(II), cobalt(II) and nickel(II) Complexes. All of the complexes featuring the bulky chlorido ligand are five coordinate, with a (distorted) trigonal bipyramidal 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 the Jahn–Teller effect. The geometry of the nickel complex is more distorted than that of iron, which is likely a result of the smaller atomic radius of the nickel atom. The two-electron reduction of the nickel complex is more distorted than that of iron, which is distorted as a result of the Jahn–Teller effect. The geometry of the cobalt complex is the most distorted as a result of the Jahn–Teller effect.

Experimental Section

General Methods: All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques or in the glovebox. Reagents were purchased from commercial suppliers and used without further purification. THF, pentane, hexane and Et2O were distilled from sodium benzophenone ketyl, CH2Cl2 was distilled from CaH2 under nitrogen. NMR spectra [1H, 31P, and 13C(1H, 31P)] were measured on a Bruker DRX 500, Bruker AV 400, Bruker DRX 300 or on a Bruker AV 300 spectrometer. IR spectra (ATR mode) were recorded with a Bruker Alpha-p FT-IR spectrometer. High resolution mass spectra were recorded on a JEOL AccuTOF LC, JMS-T100LP mass spectrometer using cold electron-spray ionization (CSI) at –40 °C. 1H, 13C, and 31P NMR spectra at 2018 cm–1) within 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.

Table 5. Selected bond lengths and angles of the FeClL1H (14), FeClL2H (15), FeClL3Pr (16) and Fe(N2)L1H (9) complexes.

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>FeClL1H (14)</th>
<th>FeClL2H (15)</th>
<th>FeClL3Pr (16)</th>
<th>Fe(N2)L1H (9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1–P1</td>
<td>2.2214(9)</td>
<td>2.2577(9)</td>
<td>2.3439(9)</td>
<td>2.1537(12)</td>
</tr>
<tr>
<td>Fe1–P2</td>
<td>2.2045(9)</td>
<td>2.2331(7)</td>
<td>2.2448(9)</td>
<td>2.1611(13)</td>
</tr>
<tr>
<td>Fe1–P3</td>
<td>2.1970(9)</td>
<td>2.2372(7)</td>
<td>2.2563(9)</td>
<td>2.1601(13)</td>
</tr>
<tr>
<td>Fe1–P4</td>
<td>2.1137(9)</td>
<td>2.0448(7)</td>
<td>2.0951(8)</td>
<td>2.1295(12)</td>
</tr>
<tr>
<td>Fe1–C1</td>
<td>2.3003(9)</td>
<td>2.2869(7)</td>
<td>2.3024(8)</td>
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<tr>
<td>Fe1–N1</td>
<td></td>
<td></td>
<td>1.818(4)</td>
<td></td>
</tr>
<tr>
<td>N1–N2</td>
<td></td>
<td></td>
<td>1.118(3)</td>
<td></td>
</tr>
<tr>
<td>P1–Fe1–P2</td>
<td>131.87(4)</td>
<td>134.19(3)</td>
<td>130.12(3)</td>
<td>120.76(3)</td>
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<tr>
<td>P1–Fe1–P3</td>
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<td>109.11(3)</td>
<td>114.44(3)</td>
<td>116.69(5)</td>
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<td>P2–Fe1–P3</td>
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<td>111.60(3)</td>
<td>112.53(3)</td>
<td>120.70(5)</td>
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<tr>
<td>P1–Fe1–P4</td>
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<td>83.81(3)</td>
<td>83.29(3)</td>
<td>85.87(5)</td>
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<td>P2–Fe1–P4</td>
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<td>80.81(3)</td>
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<tr>
<td>P3–Fe1–P4</td>
<td>85.76(3)</td>
<td>83.45(3)</td>
<td>84.67(3)</td>
<td>85.59(5)</td>
</tr>
<tr>
<td>C11–Fe1–P4</td>
<td>177.15(4)</td>
<td>169.87(3)</td>
<td>175.37(4)</td>
<td>178.04(12)</td>
</tr>
</tbody>
</table>

Figure 12. Displacement ellipsoid plot of FeN2L1H (9) (50 % probability ellipsoids) (CCDC 1579215). Hydrogen atoms and THF solvent molecule have been omitted for clarity.
[FeCl₄]⁻ 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.[20]

**Tris-2-(3-methyl-η-diisopropylphosphinoindolyl)phosphine (L₃₈P̈):** 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. nBuLi (2.5 M in hexanes; 2.9 mL; 19.44, 13.54, 9.03, 6.29, 2.67 (s, 9 H) ppm.31P NMR (121 MHz, CDCl₃): δ = 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 [NiClL₁H⁺][NiCl₄] results in the formation of crystals suitable for X-ray diffraction analysis. Mass Analysis (CS-ESI) [NiClL₁H⁺]: found: 1066.2097 calcd.: 1066.2075; BF₄⁻: found: 87.0049, calcd.: 87.0029.

**[FeClL₁H⁺][BF₄] (2b):** Compound L₁H₄ (94.9 mg; 0.097 mmol; 1.0 equiv.), NaBF₄ (10.7 mg; 0.097 mmol; 1.0 equiv.) and NiCl₂·6H₂O (23.1 mg; 0.097 mmol; 1.0 equiv.) were 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 %).1H NMR (300 MHz, CDCl₃): δ = 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.13C NMR (121 MHz, CDCl₃): δ = 10.94 (d, J = 49.2 Hz, 3 H), 17.2 (s, 3 H), 21.2 (s, 3 H), 21.1 (s, 3 H), 27.6 (s, 3 H), 31.2 (s, 3 H) ppm.19F NMR (376 MHz, CDCl₃): δ = –139.65 (m, Cq), 136.03 (m, Cq), 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 (CS-ESI) [NiClL₁H⁺]: found: 1066.2097 calcd.: 1066.2075; BF₄⁻: found: 87.0049, calcd.: 87.0029.

**[FeClL₁H⁺][BF₄] (3):** Compound L₁H₄ (105.5 mg; 1.08 mmol; 1.1 equiv.), NaBF₄ (150 mg; 1.18 mmol; 1.1 equiv.) and FeCl₂ (118 mg; 1.08 mmol; 1.0 equiv.) were suspended in THF (40 mL) and stirred overnight. The purple reaction mixture was evaporated in vacuo and extracted with CH₂Cl₂ (100 mL). The purple solution was filtered, evaporated, dissolved in THF (3 × 10 mL) and the solvents evaporated to dryness to remove the residual CH₂Cl₂. The solid was washed with Et₂O (3 × 5 mL) and dried 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 FeCl₂·4H₂O with pentane. 1H NMR (300 MHz, CDCl₃): δ = 6.29 (d, J = 168.7 Hz, 3 P), –77.94 (q, J = 168.8 Hz, 1 P) ppm.13C{1H} NMR (121 MHz, CDCl₃): δ = 185.01, 139.06, 138.79, 138.73, 138.70, 138.68, 138.66, 138.63, 138.61, 138.59, 138.57, 138.55, 138.53, 138.51, 138.49, 138.47, 138.45 ppm.19F NMR (376 MHz, CDCl₃): δ = –139.65 (m, Cq), 136.03 (m, Cq), 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 (CS-ESI) [FeClL₁H⁺]: found: 1064.2105 calcd.: 1064.2073; BF₄⁻: found: 87.0000, calcd.: 87.0029.

**[FeClL₁H⁺][BF₄] (4):** Compound L₁H₄ (7): Compound L₃₈P̈ (0.523 g; 0.68 mmol; 1.0 equiv.), NaBF₄ (0.082 g; 0.74 mmol; 1.1 equiv.) and FeCl₂ (0.178 g; 1.36 mmol; 2.1 equiv.) were suspended in THF (10 mL) and stirred for three days. The reaction mixture was evaporated to dryness, washed with pentane (5 × 10 mL) and extracted with CH₂Cl₂ (100 mL). The purple solution was filtered, evaporated, dissolved in THF (3 × 10 mL) and evaporated 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. Csl mass analysis showed that the product was a mixture of FeCl₂·4H₂O[FeL₁H⁺][FeCl₄]·[FeCl₄], but the exact ratio could not be determined. Mass Analysis (CS-ESI) [FeClL₁H⁺]: found: 860.2963 calcd.: 860.3012. BF₄⁻: found: 87.0049; [FeCl₄]: found: 160.8455; [FeCl₄]: 197.8139. Mass Analysis (CS-ESI) [FeClL₁H⁺]: found: 1064.2105 calcd.: 1064.2073; BF₄⁻: found: 87.0000, calcd.: 87.0029. Reactions of L₁OMe with L₁CF₃ and L₁H₄ with FeCl₂ were performed in a similar way as [FeClL₁P₃][BF₄][FeCl₄] leading to complexes 4, 5, 6 and 7 as mixtures of the [FeClL₁P₃]+ with unknown amounts of BF₄ and FeCl₄. These mixtures were used as such for the reduction to the FeN₄L complex and the in situ analysis of the N₂ stretch frequency using infrared spectroscopy.
[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. 13P NMR (121 MHz, CD3CN): δ = 116.77 (q), 97.59 (t, J = 44.2 Hz), 56.18 (q) ppm. The 15N-CMR spectrum could not be obtained in pure form. 19F NMR (282 MHz, CD3CN): δ = 151.10 ppm. Mass analysis (CSI) [FeL1H]+: found: 1048.2362 calcd.: 1048.2369; BF4−: 44.2 Hz), 56.18 (q) ppm. The 13C-NMR spectrum could not be obtained free of graphic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: Iron · Cobalt · Nickel · Dinitrogen complexes · P ligands