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

van de Watering, F.F.; Stroek, W.; van der Vlugt, J.I.; de Bruin, B.; Dzik, W.I.; Reek, J.N.H.

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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 PPPh₃ = P(CH₂CH₂PPh₂)₃ or PPiPr₃ = [P(CH₂CH₂PiPr₂)₃] coordinated to iron(II), cobalt(II) and nickel(II) have been exten-

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.

[a] Homogeneous, Supramolecular and Bio-Inspired Catalysis, Van ‘t Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH, Amsterdam, The Netherlands
E-mail: J.N.H.Reek@uva.nl
wdzik@wp.pl
http://www.uva.nl/en/profile/r/e/j.n.h.reek/j.n.h.reek.html

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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 (\(\text{L}^1\)) 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 (\(\text{L}^1\), \(\text{L}^2\) and \(\text{L}^3\)) 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 \(^{31}\text{P}\) NMR spectroscopy. Cold Spray Electron Ionization Mass Spectroscopy (CS-ESI-MS) revealed the presence of \(\text{NaBF}_4\) (Figure 1) with the sodium cation acting as the scavenger of the formation of a pentacoordinate \([\text{Co}(\text{Cl})\text{L}^1]^+\) cation which pointed to the possibility of multidentate molecules, which possess a very distorted geometry around the metal center, almost in-between a trigonal bipyramidal and square pyramidal geometry (\(\tau\#1 = 0.55\) and \(\tau\#2 = 0.67\)).\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 \([\text{RhClL}^1]^\text{PF}_6\) \((\tau = 0.55)\).\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.

CS-ESI mass spectroscopy analysis showed the presence of the \([\text{Co(Cl)L}^1]^+\) cation in both \([\text{Co(Cl)L}^1]^+\text{BF}_4\) (1b) and \([\text{Co(Cl)L}^1]^+\text{[CoCl}_4]\) (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 \([\text{Co(Cl)L}^1]^+\text{[CoCl}_4]\) shows an extra signal (700–2500 G) corresponding to the high spin tetrachlorido cobaltate anion, which is absent in the \([\text{CoL}^1]^\text{BF}_4\).

Layering a dichloromethane solution of \([\text{Co(Cl)L}^1]^+\text{[CoCl}_4]\) with pentane resulted in the formation of single crystals suitable for X-ray diffraction analysis (Figure 3). As expected, the binary complex \([\text{Co(Cl)L}^1]^+\text{[CoCl}_4]\) \((1\text{a})\) is present in the crystal structure. The two \([\text{Co(Cl)L}^1]^+\) 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 \(r_{578} = 0.67)\).\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 \([\text{RhClL}^1]^\text{PF}_6\) \((\tau = 0.55)\).\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.

Results and Discussion

Formation of Mono and Binary Cobalt \(\text{L}^1\) Complexes

We started our investigations with coordination studies of the tripodal indolyl-based tetraphosphine ligand (\(\text{L}^1\)) to cobalt(II). Stoichiometric amounts of \(\text{L}^1\) and \(\text{CoCl}_2\cdot6\text{H}_2\text{O}\) in THF did not lead to full consumption of \(\text{L}^1\) as judged by in situ \(^{31}\text{P}\) NMR spectroscopy. Cold Spray Electron Spray Ionization Mass Spectroscopy (CS-ESI-MS) revealed the presence of \(\text{CoCl}_4^{2–}\) dianion which pointed to the possibility of the formation of a pentacoordinate \([\text{Co(Cl)L}^1]^+\text{[CoCl}_4]\) (1a) complex in which a part of the \(\text{CoCl}_2\) 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 \(\text{L}^1\) with \(\text{CoCl}_2\) in a 2:3 stoichiometry to quantitatively form the binary \([\text{Co(Cl)L}^1]^+\text{[CoCl}_4]\) complex 1a. The monometallic complex could be obtained when the reaction was carried out in the presence of \(\text{NaBF}_4\) (Figure 1) with the sodium cation acting as the scavenger of one of the chloride anions. This led to clean formation of \([\text{CoL}^1]^\text{BF}_4\) (1b) from stoichiometric amounts of \(\text{L}^1\) and \(\text{CoCl}_2\cdot6\text{H}_2\text{O}\) in THF.

Figure 2. EPR spectra of \([\text{Co(Cl)L}^1]^+\text{BF}_4\) (green line) and \([\text{Co(Cl)L}^1]^+\text{[CoCl}_4]\) (blue line) measured in frozen THF at 20 K (Bu\(_4\)NF\(_6\) was added to obtain a better glass). Experimental parameters: microwave frequency 9.389 GHz, microwave power 0.632 mW, modulation amplitude 4 G.

![Figure 2](image-url)
Figure 3. Displacement ellipsoid plot of [Co(Cl)L1H][CoCl4] (1a) (50% probability ellipsoids) (CCDC 1579207). Dichloromethane solvent molecules, phenyl rings and hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths and angles of the [Co(Cl)L1H][CoCl4] (1a) and [Ni(Cl)L1H][NiCl4] (2a) complexes.

<table>
<thead>
<tr>
<th></th>
<th>[Co(Cl)L1H][CoCl4] (1a)</th>
<th>[Ni(Cl)L1H][NiCl4] (2a)</th>
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<tr>
<td></td>
<td>[Co(Cl)L1H]+ #1</td>
<td>[Co(Cl)L1H]+ #2</td>
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<tr>
<td>M1–P1</td>
<td>2.2422(11)</td>
<td>2.2691(11)</td>
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<td>M1–P2</td>
<td>2.2590(11)</td>
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<td>2.2673(11)</td>
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<td>M1–P4</td>
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<td>137.07(4)</td>
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<td>109.62(4)</td>
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<tr>
<td>P2–M1–P3</td>
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<td>111.72(4)</td>
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<td>P1–M1–P4</td>
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<td>85.26(4)</td>
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<tr>
<td>P2–M1–P4</td>
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<td>86.23(4)</td>
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<tr>
<td>P3–M1–P4</td>
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<td>86.38(4)</td>
</tr>
<tr>
<td>Cl1–M1–P4</td>
<td>173.63(5)</td>
<td>177.33(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 ($\delta = 61.06$ ppm) and one quartet ($\delta = 25.91$ 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, and trigonal bipyramidal geometry was also reported for the d8 [Ru(N2)L1H][23] and the [Pd(Cl)L1H][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

Figure 4. Displacement ellipsoid plot of [Ni(Cl)L1H][NiCl4] (2a) (50% probability ellipsoids) (CCDC 1579208). Dichloromethane solvent molecules, phenyl rings and hydrogen atoms have been omitted for clarity.
[Ni(Cl)L1^t]^+ ion in both [Ni(Cl)L1^t]BF4 (2b) and [Ni(Cl)L1^t]-[NiCl4] (2a) (see experimental section). Slow diffusion of hexane to a dichloromethane solution of [Ni(Cl)L1^t][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)L1^t][NiCl4] complex 2a where the two [Ni(Cl)L1^t]^+ units crystallize as two independent molecules. The [Ni(Cl)L1^t]^+ units feature a distorted trigonal bipyramidal geometry around the metal center (τ5#1 = 0.70 and τ5#2 = 0.86) (Table 1).[41] The geometry is less distorted than the geometry of the cobalt analogues (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–P3 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 tetradentate indolyl phosphate ligand L1^t 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^t(Cl)L1^t]^+ 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 L1^t ligand complexes are pentacoordinate, 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,[23,24] 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 phosphate ligands. The reaction of FeCl2 with L1^t in THF in a 1:1:1 stoichiometry led to full conversion of the counterion respectively, which is in accordance with a five-coordinate iron(II) complex.

The new ligand was prepared by reacting the lithium salt PrL1CF3 with FeCl2 in THF in a 1:1:1 stoichiometry. DFT calculations suggest that the lowest energy state of the [Fe(Cl)L1^t]^+ cation is an intermediate spin, paramagnetic trigonal bipyramidal complex,[44] iron(II) (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)L1^t]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 tetraphosphate TBP iron(II) complexes.[10,11,19,28,37,46] 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.[41]

![Figure 5. Displacement ellipsoid plot of [Fe(Cl)L1]^+BF4 (3b) (50 % probability ellipsoids) (CCDC 1579209). Dichloromethane solvent molecule and hydrogen atoms and the BF4^- counterion have been omitted for clarity.](image)

<table>
<thead>
<tr>
<th>[Fe(Cl)L1^t]BF4 (3b)</th>
<th>[Fe(Cl)L3^t][FeCl4]2 (7)</th>
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<tr>
<td>[Fe(Cl)L1^t]^+</td>
<td>[Fe(Cl)L3^t][FeCl4]2</td>
</tr>
<tr>
<td>M1–P1</td>
<td>2.2721(9)</td>
</tr>
<tr>
<td>M1–P2</td>
<td>2.2765(10)</td>
</tr>
<tr>
<td>M1–P3</td>
<td>2.2748(9)</td>
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<tr>
<td>M1–P4</td>
<td>2.1952(8)</td>
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<td>M1–P6</td>
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<td>M2–P4</td>
<td>83.36(3)</td>
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<td>M2–P5</td>
<td>83.96(4)</td>
</tr>
<tr>
<td>C1–M1–P4</td>
<td>178.58(4)</td>
</tr>
</tbody>
</table>

Subsequently, we explored the coordination of FeCl2 to the PP3 ligands L1^tCF3, L1^tOMe, L2^tH, and L3^tPr in the presence of NaBF4 (Figure 6) to form complexes 4, 5, 6, and 7, respectively. The new ligand L3^tPr was prepared by reacting the lithium salt of tris-2-(3-methylindolyl)phosphine[47] with disopropyl chlorophosphine. Coordination of ligands other than L1^t to iron in presence of NaBF4 did not provide the monometallic complex [Fe(Cl)L1^t]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(Cl)L]^+ cation, which indicates that the ligand does coordinate to the iron center. Analy-
sis in the negative mode showed the presence of the expected BF$_4^-$ anion but also the presence of the FeCl$_5^-$ and FeCl$_6^-$ 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 L$^{3\Pr}$ with FeCl$_2$ in the presence of 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 [FeCl$_4^-$] (likely formed in situ by a reaction of [FeCl$_4^-$]$^{2-}$ with traces of oxygen) as counterion, resulting in the binary [Fe[Cl][L$^{3\Pr}$][FeCl$_4^-$] complex 7 (Figure 7).

Figure 7. Displacement ellipsoid plot of [Fe[Cl][L$^{3\Pr}$][FeCl$_4^-$] (7) (50% probability ellipsoids) (CCDC 1579210). Hydrogen atoms and the FeCl$_4^-$ counterion have been omitted for clarity. The crystal of [Fe[Cl][L$^{3\Pr}$][FeCl$_4^-$] reveals the presence of two independent [Fe[Cl][L$^{3\Pr}$]$^+$ cations and two independent [FeCl$_4^-$] anions in the asymmetric unit.

[Fe[Cl][L$^{3\Pr}$][FeCl$_4^-$] (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 ($\tau$$_{5\Pr}$$^1$ = 0.95 and $\tau$$_{5\Pr}$$^2$ = 0.98) (Table 1).$^{[41]}$ The P1–Fe1, P2–Fe1 and P3–Fe1 bond lengths are elongated compared to the [Fe[Cl][L$^{1H}$]$^+$ unit, which is likely a result of the more electron-donating diisopropylphosphine groups. The other angles and distances are comparable to the [Fe[Cl][L$^{1H}$]$^+$ unit and values reported in literature.$^{[19,28,46]}$

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 L$^{1H}$ to Fe(BF$_4$)$_2$ (Figure 8).

Stirring of stoichiometric amounts of L$^{1H}$ and Fe(BF$_4$)$_2$ in 1:1 (v/v) THF/toluene mixture at 70 °C for three days led to precipi-
Attempts to synthesize iron(+II) complexes with ligands \( \text{L}^1 \text{Cl}^2 \text{P}^3 \) and \( \text{L}^1 \text{OME}^1 \), 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 \( \text{N}_2 \) 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 \( \text{N}_2 \).

**Reduction of \([\text{Co(Cl)]L}^1\text{H}]\text{BF}_4\)**

In order to gain insight in the reduction potentials needed for the cobalt complexes to form the hypothetical Co\(^0\) \( \text{L}^1\text{H}^4 \) \( \text{N}_2 \) complex, the \([\text{Co(Cl)]L}^1\text{H}]\text{BF}_4\) (1b) complex was analyzed electrochemically. The CV of this cobalt complex shows one reversible redox couple \((E^{1/2} = -0.56 \text{ V vs. Fc/Fc}^+),\) below which Co\(^0\) complex \([\text{Co(L1H)}]\text{BF}_4\) is reduced to Co\(^+\) complex \([\text{Co(L1H)}]^{-}\) (see the Supporting Information). This value is slightly more negative than for the reversible Rh\(^0\)/Rh\(^+\) couple of the rhodium \([\text{Rh(Cl)]L}^1\text{H}]\text{PF}_6\) analogue \((E^{1/2} = -0.4 \text{ V vs. Fc/Fc}^+),\)\(^{20}\) and comparable to the reversible \( \text{Co}^{0}/\text{Co}^{1} \) couple of the \([\text{Co(PPPh}_3^1]^{-}\) \( \text{NH}_2\text{CN}^{-}\rangle\) \( \text{BF}_4^{-}\) complex \((E^{1/2} = -0.54 \text{ V}).\)\(^{48}\) Scanning to lower potentials resulted in two non-reversible reduction peaks at very similar potentials \((E = -2.3 \text{ and } -2.4 \text{ V vs. Fc/Fc}^+).\) Likely, one of these peaks corresponds to the reduction of Co\(^0\) to Co\(^+\), which could lead to binding of the dinitrogen to the cobalt center. Consequently, we also tried to reduce the \([\text{Co(L1H)}]\text{BF}_4\) (1b) complex chemically. The chemical reduction of the \([\text{Co(L1H)}]\text{BF}_4\) complex with 2 equiv. of KC\(_8\) in the presence of \( \text{N}_2 \) was monitored by IR spectroscopy. The IR spectra did not show a signal corresponding to the dinitrogen stretch frequency typical for an \( \text{N}_2 \) coordination complex. In addition, in situ analysis of the reaction mixture by \( ^{31} \text{P} \) NMR spectroscopy showed signals indicative of ligand decomposition. Ligand decomposition may be responsible for the second reduction peak observed in the CV \((E = -2.4 \text{ V vs. Fc/Fc}^+).\) The inability of the complex to form \( \text{N}_2 \) 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 \([\text{Ni(Cl)]L}^1\text{H}]\text{BF}_4\)**

We also investigated the reduction potentials of the nickel complex using electrochemistry (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. \(Fc/Fc^+\). In addition, two non-reversible reduction peaks were observed (\(E = -2.0\ V\) vs. \(Fc/Fc^+\) and \(E = -2.5\ V\) vs. \(Fc/Fc^+\)). CV measurements of \([Ni(PPPh_3)(CH_3CN)](BF_4)_2\) showed only one reversible redox couple \(E_{1/2} = -1.03\ V\) vs. \(Fc/Fc^+\); likely the \(Ni^{II}/Ni^0\) couple) and one non-reversible reduction peak, \(E_{1/2} = -1.28\ V\) vs. \(Fc/Fc^+\); likely the \(Ni^0/Ni^{+}\) couple). The chemical potential is much lower than the earlier mentioned paramagnetic \([Fe(Cl)PPPh_3]BF_4\) (–1.9 V vs. \(Fc/Fc^+\)), corresponding to the \(Fe^{III}/Fe^{II}\) and \(Fe^{II}/Fe^0\) couple respectively. The latter \(Fe^{II}/Fe^0\) reduction potential is much lower than the earlier mentioned paramagnetic \([Fe(Cl)PPPh_3]BF_4\) complex of Bianchini (–1.0 V vs. \(Fc/Fc^+\)) in 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 \([Fe(Cl)L^{1H}]BF_4\)

Next, we investigated whether it was possible to reduce the \([Fe(Cl)L^{1H}]BF_4\) (3) complex electrochemically. The cyclic voltammogram (see Figure S19) of \([Fe(Cl)L^{1H}]BF_4\) (3) in THF shows two reversible redox couples, one at \(E_{1/2} = -0.38\ V\) vs. \(Ag/AgCl\) (–0.96 V vs. \(Fc/Fc^+\)) and one at \(E_{1/2} = -1.29\ V\) vs. \(Ag/AgCl\) (–1.9 V vs. \(Fc/Fc^+\)), corresponding to the \(Fe^{II}/Fe^0\) and \(Fe^0/Fe^{II}\) couple respectively. The latter \(Fe^0/Fe^{II}\) reduction potential is much lower than the earlier mentioned paramagnetic \([Fe(Cl)PPPh_3]^+\) complex of Bianchini (\(E_{1/2} = -0.64\ V\) vs. \(Ag/AgCl\)). Like Bianchini’s complex, the reduction of \(Fe^0\) 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 \([Fe(Cl)L^{1H}]BF_4\) (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 \(Fe(N_2)L^{1H}(9)\) 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 \(KC_8\).

Reduction of Other Iron(II)CIPP₃ Complexes

The in situ formed iron(0)\(N_2\)CIPP₃ 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 \(Fe(N_2)L^{2H}\) complex 12 has the highest \(N_2\) stretch frequency (\(\nu_{N_2} = 2068\ cm^{-1}\)) and \(Fe(N_2)L^{3Pr}\) (13) has the lowest \(N_2\) stretch frequency (\(\nu_{N_2} = 2018\ cm^{-1}\)) in the infrared spectrum.

As expected, the extent of activation of \(N_2\) by iron complexes with the 3-methylindole based tetraphosphine ligands \(L^{1H}\), \(L^{1CF3}\), \(L^{1OMe}\) and \(L^{2H}\) is higher than for the analogous rhenium complexes.\(^{[23]}\) The increase of the electron donating capacity of the substituents of the equatorially coordinated phosphines when going from \(L^{1CF3}\) to \(L^{3Pr}\) 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 the \(\pi\)-acidity of the donors trans to molybdenum-coordinated \(N_2\) by Tuczek 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.\(^{[49]}\) 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 \(Fe^0(N_2)\) trans to \(P(CH_2CH_2PPh_3)_{13}\) (\(\nu_{N_2} = 1985\ cm^{-1}\)) as reported by the groups of George and Zubieta\(^{[50]}\) and Field,\(^{[19]}\) respectively.

Figure 10. Two-electron reduction of iron(II) complexes with 3-methylindole-based tripodal tetraphosphine ligands in the presence of \(N_2\).
Compared to the iron complexes with tripodal tetradeionate 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(BPᵢPr₃)N₂,[52] [Fe₀(CPᵢPr₃)N₂]–,[53] [Fe₀(SiPᵢPr₃)N₂]–,[52] reveal νN₂ = 2011 cm⁻¹, 1870 cm⁻¹ and 1891 cm⁻¹ respectively. Since ligands CPᵢPr₃ and SiPᵢPr₃ 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 L₃ᵢPr complex. However, the overall donating capability of BPᵢPr₃ (which is the most effective tripodal system for N₂ activation[15]) to iron is similar to L₃ᵢPr. The major difference between BPᵢPr₃ and the 3-methylindolyl-based ligand systems presented in this work is the capability of BPᵢPr₃ to accommodate a negatively charged [Fe⁻¹(N₂)L]– complex upon one electron reduction of the neutral Fe(N₂)L, resulting in further weakening of the N–N bond (νN₂ = 1905 cm⁻¹), and rendering this complex an active catalyst for ammonia formation. The stabilization of such Fe⁻¹ species is possible thanks to the incorporation of the σ-acidic boron atom in the BPᵢPr₃ ligand. Unfortunately, the addition of one extra equivalent of KC₈ to Fe₀(N₂)PP₃ 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)L₁H¹⁺ (14), Fe(Cl)L₂H¹⁺ (15) and Fe(Cl)L₃ᵢPr¹⁺ (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) complex, indicating that the reduction reactions intended to form Fe⁰N₂L did not go to completion, and besides the desired iron(0) species also iron(+I) complexes are formed. As expected for a d⁷ 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)L₁H¹⁺ (τ₅ = 0.75), Fe(Cl)L₂H¹⁺ (τ₅ = 0.69) and Fe(Cl)L₃ᵢPr¹⁺ (τ₅ = 0.75) (Table 5).

Upon addition of a slight excess of KC₈ to the [Fe(Cl)L₁H₄]BF₄ 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(N₂)L₁H (9) complex formed that were suitable for X-ray diffraction analysis (Figure 12). The crystal structure of Fe(N₂)L₁H reveals a nearly ideal trigonal bipyramidal geometry around the metal center (τ₅ = 0.95).[14] The structure is more symmetrical than the iron(+II) and ruthenium(0) analogues, but structurally comparable to the known Fe(N₂)(PPᵢPr₃) (νN₂ = 1985 cm⁻¹) complex.[19] The N–N bond length of FeN₂L₁H is slightly shorter [1.118(5) Å] than in FeN₂(PPᵢPr₃) [1.1279(16) Å], which is in accordance with a less activated N₂ moiety in Fe(N₂)L₁H. These experiments therefore show that electronic variation in the ligands that coordinate to the iron metal have a clear effect on the activation of N₂ bound to Fe.
Table 5. Selected bond lengths and angles of the FeCLiH (14), FeCL2H (15), FeCL3PP (16) and FeNL1H (9) complexes.

<table>
<thead>
<tr>
<th></th>
<th>FeCLiH (14)</th>
<th>FeCL2H (15)</th>
<th>FeCL3PP (16)</th>
<th>FeNL1H (9)</th>
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<tr>
<td>Fe1–P1</td>
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<td>2.3439(9)</td>
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<td>Fe1–P2</td>
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<td>2.0448(7)</td>
<td>2.0951(8)</td>
<td>2.1295(12)</td>
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<tr>
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<td>2.2869(7)</td>
<td>2.3024(8)</td>
<td>2.3006(8)</td>
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<tr>
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<td>1.818(4)</td>
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<td>P1–Fe1–P2</td>
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<td>169.87(3)</td>
<td>175.37(4)</td>
<td>178.04(12)</td>
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</tbody>
</table>

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 non-coordinating counterion, which can be either BF4\(^{-}\) or [MCl4]\(^{2-}\). In addition, one octahedral iron PP3 complex was prepared, which features two 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 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 compared to iron atom. The two-electron reduction of the cobalt(II) and nickel(II) complex in the presence of N2 did not lead to the coordination of N2. 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: The complex Fe(N2)L2+[Fe(N2)L2]+ featuring the most \(\pi\)-acidic phosphorus donor \(trans\) to the coordinated N2 ligand has the highest IR stretch frequency (\(\nu_{N2} = 2068 \text{ cm}^{-1}\)) while introduction of strongly s-donating groups in complex Fe(N2)L3PP resulted in the lowest IR stretch frequency (\(\nu_{N2} = 2018 \text{ cm}^{-1}\)) 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)] were measured on a Bruker DRX 300, 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. L1H[21], L2F3[24], L1OMe[24] and L2H2[24] were prepared in two steps from 3-methylindole. KC8 was prepared by the method of Weitz and Rabinovitz. Experimental X-band EPR spectra were recorded on a Bruker EMX spectrometer equipped with a He temperature control cryostat system (Oxford Instruments). Crystallographic data was obtained using a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator and a Photon 50 detector. The intensities were integrated with the SAINT software package. Multiscan absorption correction and scaling was performed with SADABS. The structure was solved with Intrinsic Phasing Methods using SHELXT. Least-squares refinement was performed with SHELXL 2013 against \(F^2\) of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. Structures of [Co(CL1H)][CoCl4], [Ni(CL1H)][NiCl4], [Fe(MeCN)L1H(BF4)2] and [Fe(CL3PP)]...
FeCl3 have solvoly 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.10,19

Tris-2-(3-methyl-1119-diisopropylphosphinooindolyl)phosphine (L3[P]): Tris-2-(3-methylindinyl)phosphine (1.02 g; 2.42 mmol; 1.0 equiv.) was dissolved in THF (50 mL) and cooled to –78 °C. To 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, chlorodisopropylphosphine (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 and dried in vacuo yielding the product in pure form as a white powder (0.83 g; 45 % yield).

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. 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 [NiCl2·(L3[P])]2+[NiCl4]– resulted in crystals suitable for X-ray diffraction analysis. Mass Analysis (CS-ESI) [NiCl(L3)[BF4]2]: found: 769.3984, calcd.: 769.3972.

[Fe(EDTA)]6H2O (38.2 mg; 0.16 mmol; 1.0 equiv.) were suspended in 20 mL chloromethane solution with pentane at 5 °C. CSI mass analysis showed that the product was a mixture of [Fe(EDTA)]6H2O, but the exact ratio could not be determined. Mass Analysis (CS-ESI) [Fe(EDTA)6H2O]: found: 860.2963, calcd.: 860.3012. BF4–: found: 87.0049; [Fe(EDTA)6]: found: 160.8455; [FeCl3]: found: 197.8139.

Reactions of FeCl2 (0.178 g; 1.36 mmol; 2.1 equiv.) were suspended in THF (15 mL) and cooled to –78 °C. To this was added nBuLi (1.04 mL; 1.52 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 FeCl3BF4 with pentane. 1H NMR (300 MHz, CDCl3): δ = 16.24 (bs), 14.74 (bs), 8.87 (bs), 8.35 (bs), 3.13 (bs), –0.37 (bs), –8.30 (bs), –9.14 (bs) ppm. UV/Vis (THF) λmax: 553 nm. Mass Analysis (CSI) [FeCl(L1)H]: found: 1064.2105 calcd.: 1064.2073; BF4–: found: 87.0000, calcd.: 87.0029.

[FeCl(L1)BF4]2 (2b): Compound L1H+ (94.9 mg; 0.097 mmol; 1.0 equiv.), NaBF4 (107 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 = 7.21 (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. 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. 13C{1H,31P} NMR (75 MHz, CDCl3): δ = 139.65 (m, Cq), 136.03 (m, Clq), 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) [NiCl(L1)H]+: found: 1066.2097 calcd.: 1066.2075; BF4–: found: 87.0049, calcd.: 87.0029.

[FeCl(L3)BF4]2 (3b): Compound L3+ (1.05 g; 1.08 mmol; 1.0 equiv.), NaBF4 (150 mg; 1.18 mmol; 1.1 equiv.) and FeCl3 (118 mg; 1.08 mmol; 1.0 equiv.) were suspended in THF (40 mL) and stirred overnight. The purple precipitate was filtered off, washed with Et2O and 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 FeCl3BF4 with pentane. 1H NMR (300 MHz, CDCl3): δ = 16.24 (bs), 14.74 (bs), 8.87 (bs), 8.35 (bs), 3.13 (bs), –0.37 (bs), –8.30 (bs), –9.14 (bs) ppm. UV/Vis (THF) λmax: 553 nm. Mass Analysis (CSI) [FeCl(L1)H]: found: 1064.2105 calcd.: 1064.2073; BF4–: found: 87.0000, calcd.: 87.0029.

[FeCl(L3)BF4]2(BF4)2 (7): Compound L3+ (0.523 g; 0.58 mmol; 1.0 equiv.), NaBF4 (0.082 g; 0.74 mmol; 1.1 equiv.) and FeCl3 (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 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. Mass analysis showed that the product was a mixture of [FeCl3(L3)][BF4]2, but the exact ratio could not be determined. Mass Analysis (CS-ESI) [FeCl(L1)H]+: found: 860.2963, calcd.: 860.3012. BF4–: found: 87.0049; [FeCl3]: found: 160.8455; [FeCl3]: found: 197.8139.

Reactions of L1OMe and L1CF3 and L2H with FeCl3 were performed in a similar way as [FeCl3(L3)][BF4]2[FeCl3], leading to complexes 4, 5, 6 and 7 as mixtures of the [FeCl3]+ with unknown amounts of BF4 and FeCl3. These mixtures were used as such for the reduction to the FeN2 and the in situ analysis of the N2 stretch frequency using infrared spectroscopy.
[Fe(MeCN)₂L₁H](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, CD₂CN): 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 ¹¹B NMR spectrum could not be obtained in pure form. ¹⁹F NMR (282 MHz, CD₃CN): δ = 151.10 ppm. Mass analysis (CSI) [FeL₁H⁺]: found: 514.6169, calcld.: 514.6192; [FeL₁H₂⁺]: found: 1048.3262 calcld.: 1048.3269; BF₄⁻: found: 87.0049, calcld.: 87.0029.

**Standard Procedure for the Reduction of the Complexes with K₃[C₈]:** 20 mg of the complex was suspended with 2–5 equiv. of K₃[C₈] 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 methanol to the THF solution. Crystals suitable for X-ray diffraction analysis formed for complexes FeCl₉(L₁H) (for 7), 1579211 (for 8), 1579212 (16) and FeCl₉(L₁H) (9) were obtained in 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.

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


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