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# Phosphine functionalized NHC ligands and their cyclopentadienide nickel(II) complexes

Jens Trampert,[a] Marcel Nagel,[a] Tobias Grimm,[a] Yu Sun [a] and Werner R. Thiel*[a]

Dedicated to Prof Dr. Alexander C. Filippou on the occasion of his 60th birthday

**Abstract:** By reaction of phosphine functionalized imidazolium salts with nickelocene, a series of cationic 18 VE nickel(II) half-sandwich complexes have been obtained in high yields. Herein the nickel(II) centers are coordinated in a chelating fashion by the *N*-heterocyclic carbene (NHC) and the phosphine donor sites. The so obtained chelating ring can be opened by cyanide leading to neutral cyanidonickel(II) NHC complexes. Application of imidazolium salts functionalized with thiophosphine groups prevents the formation of chelate complexes. Instead neutral chloridonickel(II) NHC species are obtained.

## Introduction

In 1953 Fischer and Jira reported the synthesis of nickelocene, obtained by reacting $[Ni(NH_3)_6](SCN)_2$ with potassium cyclopentadienide in liquid ammonia.[1] As expected, the paramagnetic 20 VE complex turned out to be less stable than ferrocene. While oxidizing as well as reducing agents lead to loss of both cyclopentadienide ligands, treatment with acids allows for the splitting one of the $\eta^5$-coordinated $\pi$-donors. The resulting monocyclopentadienide nickel(II) intermediates require stabilization by other donor molecules.

The classical synthesis of the nickel(II) tripledecker cation $[Cp_3Ni_2]^+$ follows this sequence:[2] Treatment of nickelocene with $HBF_4$ splits one cyclopentadienido ligand and leaves behind the reactive $[CpNi]^+$ cation which gets stabilized by binding to another nickelocene molecule. Dinuclear nickel(II) complexes are obtained with (weak) acids containing only one donor atom such as phosphines ($HPR_2$) and sulfides (HSR) or with pyrazoles.[3,4,5] Mononuclear compounds have been obtained e. g. with phosphonates, wherein the nickel(II) site is coordinated by two phosphorus donors that are linked by an O···H···O bridge.[6] Starting from such compounds, multinuclear complexes are accessible.[7]

In the year 2000, Jones et al. were the first using the acidity of imidazolium salts to remove one of the cyclopentadienido ligands from nickelocene.[8] They obtained a 18 VE cyclopentadienidonickel(II) complex bearing a *N*-heterocyclic carbene ligand (NHC). This finding stimulated ongoing research in the area (see also refs. related to the structural discussions below).[9] However, to the best of our knowledge, no cyclopentadienidonickel(II) complexes bearing a chelating phosphine-NHC ligand were described up to now.

Phosphine functionalized imidazolium salts were introduced by Zhou et al. in 2004, who applied them in palladium catalyzed cross-coupling reactions.[10] Since then a series of catalytic applications of chelating phosphine-NHC ligands have been published, mainly concerning again palladium catalyzed C-C coupling reactions,[11] ruthenium catalyzed transfer hydrogenations [12] and iridium catalyzed C-E coupling reactions.[13] In addition, these ligands have turned out to be ideal bridging and chelating donors in cluster chemistry.[14] Recently there was one publication on the performance of cationic allyl nickel(II) complexes bearing a chelating phosphine-NHC ligand in the catalytic arylation of allylic alcohols.[15]

## Results and Discussion

Phosphine functionalized imidazolium salts used in this work were obtained following the route published by Zhou:[10] After P-C coupling with *ortho*-lithiated dimethylbenzylamine and chlorodiphenylphosphine, the resulting (*ortho*-dimethylaminomethylphenyl)diphenylphosphine was converted into the corresponding chloro derivative with ethyl chloroformate (Scheme 1). Treatment with *N*-alkylated or arylated imidazoles gave the requested imidazolium salts **1a-c** in yields of 40-60%. They are typically characterized by their $^{31}$P NMR resonances being observed at about -17 ppm. According to the short distance between the phosphorus site and the carbon atom of the methylene unit, there are large $^3J_{PC}$ couplings of approx. 22 Hz. For a better overview, Table 1 summarizes the $^{31}$P NMR chemical shifts and typical coupling constants $J_{PX}$ of the ligands and nickel(II) complexes discussed in this manuscript. The twofold phosphine functionalized imidazolium salt **1d** was accessible in approx. 60% yield by reacting sodium imidazolide or trimethylsilyl imidazole with two equivalents of the phosphine reagent in refluxing acetonitrile ($^{31}$P NMR: -16.35 ppm). **1a** and **1d** were exemplarily treated with elemental sulfur in refluxing dichloromethane, which resulted in the formation of the corresponding phosphine sulfides **1aS** and **1dS** in more than 80% yields ($^{31}$P NMR: ca. 41.5 ppm). In addition to the characteristic shift in the $^{31}$P NMR spectrum, the formation of the phosphine sulfide is confirmed by large $^1J_{PC}$ coupling constants for the couplings to the *ipso*-carbon atoms by about 80-85 Hz.

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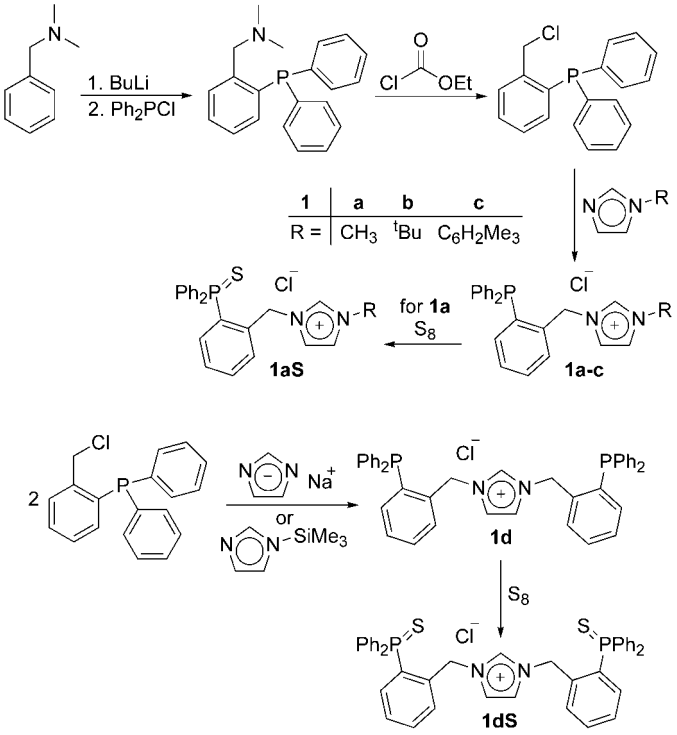



**Scheme 1.** Synthesis of the phosphine resp. thiophosphine functionalized imidazolium salts **1a-d**, **1aS** and **1dS**.

**Table 1.** Summary of typical NMR data of the free ligands and the nickel(II) complexes.

| | ligands | | | | | |
|---|---|---|---|---|---|---|
| | **1a** | **1b** | **1c** | **1d** | **1aS** | **1dS** |
| $^{31}$P δ [ppm] | -17.3 | -16.5 | -16.1 | -16.4 | 41.7 | 41.7 |
| $^{1}J_{PC}$ [a] [Hz] | 25.8 | 25.9 | 25.6 | 25.4 | 85.2 | 85.1 |
| | nickel complexes | | | | | |
| | **2a** | **2b** | **2c** | **3** | **4a** | **4b** |
| $^{31}$P δ [ppm] | 25.9 | 19.1 | 23.3 | -16.0 | 41.7 | 41.4 |
| $^{1}J_{PC}$ [a] [Hz] | 46.7 | 46.7 | [b] | 23.1 | [b] | 83.4 |
| $^{2}J_{PC}$ [c] [Hz] | 38.6 | 33.0 | 24.9 | - | - | - |

[a] coupling to the ipso carbon atoms of the phenyl rings; [b] broad signals; [c] coupling to the carbene carbon atom.

The phosphine functionalized imidazolium salts could be recrystallized by slow diffusion of diethyl ether into solutions in dichloromethane. In some cases, the chloride anions had to be exchanged against $PF_6^-$, to obtain single crystals suitable for X-ray structure analysis. Figure 1 shows exemplarily the solid-state structures of the cations of **1a** (from the $PF_6^-$ salt) and **1d**. A common feature of both structures is π-stacking between the electron-poor imidazolium ring and one of the phenyl substituents at the phosphine unit.

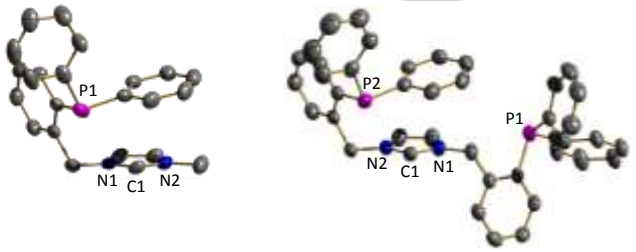
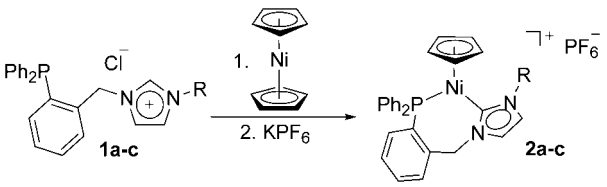



**Figure 1.** Molecular structures of the cations of **1a** (from the $PF_6^-$ salt) and **1d** in the solid state. The counter anions, hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Ellipsoids are at the 50% level.

Reacting the imidazolium salts **1a-c** with nickelocene makes accessible the nickel(II) complexes **2a-c** in good yields (Scheme 2). The chloride anion is essential for this conversion: In case imidazolium salts of weakly coordinating anions such as $PF_6^-$ or $BF_4^-$ are applied, the reaction does not take place. Obviously, chloride is necessary to help removing the proton from the imidazolium ion and to transfer it to the $Cp^-$ ligand, which finally causes CpH cleavage from the nickel(II) site. In contrast to the straightforward reactions between **1a-c** and nickelocene, that give the desired products **2a-c** without formation of any side-product, the reaction between the diphosphino functionalized imidazolium salt **1d** and nickelocene leads - by $^{31}$P NMR spectroscopy - to a complex mixture of products. At the end, the chloride anion can be exchanged against $PF_6^-$, that allows to obtain the nickel(II) complexes in crystalline form. Leaving the anion exchange process gives the corresponding chloride salts **2a-cCl** in yields of more than 90%, which show $^{1}$H and $^{13}$C NMR spectra similar to the $PF_6^-$ salts.




**Scheme 2.** Synthesis of the P,C-coordinated nickel(II) complexes **2a-c**.

The nickel(II) complexes **2a-c** could be recrystallized by slow diffusion of diethyl ether into solutions of the compounds in dichloromethane giving crystals which were suitable for X-ray structure analysis. Figure 2 shows the solid-state structures of the cations of **2a-c**.

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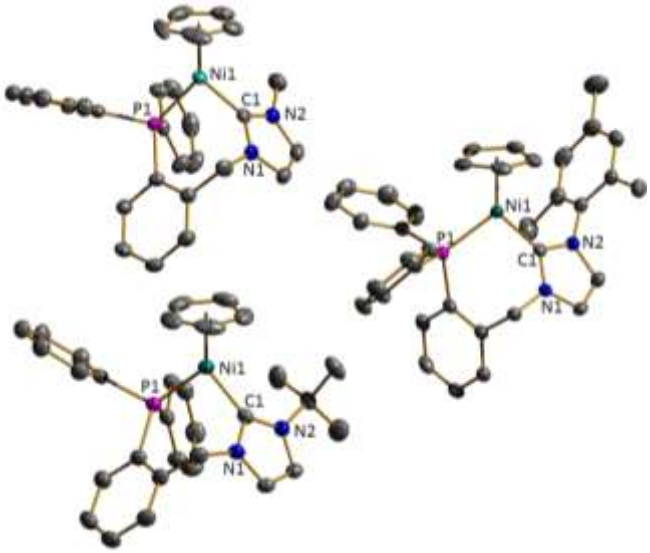
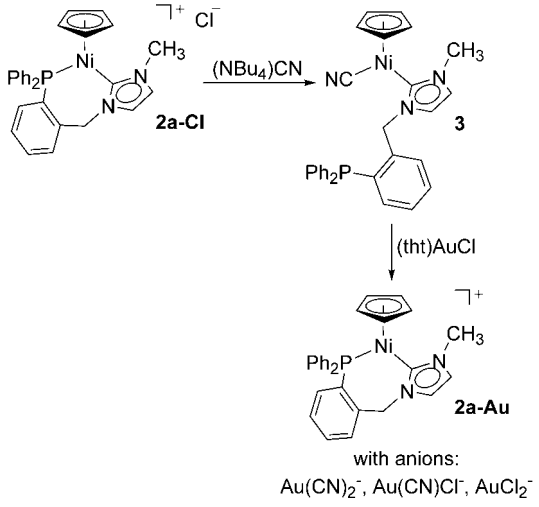



**Figure 2.** Molecular structures of the cations of **2a** (left, top), **2b** (left, bottom) and **2c** (right) in the solid state. The counter anions, hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Ellipsoids are at the 50% level. Characteristic bond lengths [Å] and angles [°]: **2a**: Ni1-P1 2.1386(6), Ni1-C1 1.877(2), Ni1-$C_{Cp}$ 2.090(2)-2.147(3), P1-Ni1-C1 89.13(6); **2b**: Ni1-P1 2.1557(6), Ni1-C1 1.910(2), Ni1-$C_{Cp}$ 2.083(3)-2.154(3), P1-Ni1-C1 92.18(6); **2c**: Ni1-P1 2.1607(8), Ni1-C1 1.904(2), Ni1-$C_{Cp}$32 2.063(2)-2.184(3), P1-Ni1-C1 99.59(7).

In general, the structural data of complexes **2a-c** are in agreement with the parameters found for other cationic CpNi(NHC) complexes.[16] However, although the three structures look quite similar, there are clear differences in their structural data resulting from the steric influence of the substituent R (Scheme 2) at the NHC moiety. The Ni-P distances increase in the series (**2a**: 2.1386(6), **2b**: 2.1557(6), **2c**: 2.1607(8) Å). The same is true for the P-Ni-C angles (**2a**: 89.13(6), **2b**: 92.18(6), **2c**: 99.59(7)°). Interestingly, the Ni-$C_{NHC}$ distance increases from **2a** (1.877(2) Å) to **2b** (1.910(2) Å), but then decreases slightly for **2c** (1.904(2) Å). According to the different *trans*-influence of the phosphine and the NHC ligand, the Ni-$C_{Cp}$ distance to the carbon atoms being in *trans*-position to the NHC ligand are significantly longer than the other ones.

The individual structural properties of the three nickel(II) complexes lead to consequences concerning their NMR spectra: Most intriguing are the large differences of the $^{13}C$ NMR chemical shifts of the carbene carbon atom (**2a**: 157.3, **2b**: 152.0, **2c**: 160.9 ppm) and of the $^{2}J_{PC}$ coupling constant (**2a**: 38.6, **2b**: 33.0, **2c**: 24.9 Hz). It therefore seems that the $^{2}J_{PC}$ coupling constant is an accurate probe for the structural situation around the P-Ni-C core of the molecules. While the $^{1}H$ and $^{13}C$ NMR spectra of **2a** and **2b**, recorded at room temperature, show rather sharp resonances, the $^{1}H$ as well as the $^{13}C$ NMR signals of **2c** are found to be partially broadened. Noticeably, line broadening is mainly restricted to the $PPh_2$ unit and - in proton NMR - to the protons of the methylene bridge, which signals are close to coalescence (**2c**: 6.33, 5.24 ppm, $^{2}J_{HH}$ 10.5 Hz). The methylene protons are diastereotopic due to the six-membered chelate ring, occupying a boat-type geometry. Therefore, two sharp doublets with large $^{2}J_{HH}$ couplings are observed for **2a** and **2b** (**2a**: 6.74, 6.09 ppm, $^{2}J_{HH}$ 14.7 Hz, **2b**: 7.68, 5.16 ppm, $^{2}J_{HH}$ 14.9 Hz). By analyzing the distance between the nickel(II) center and the methylene proton that points to the inner space of the six-membered ring (not shown in Figure 2), it becomes clear that there is another difference between the three complexes. The closer this proton comes to the nickel(II) site ($d_{NiH}$, **2a**: 2.771, **2b**: 2.665, **2c**: 2.969 Å), the more it's $^{1}H$ NMR resonance is shifted to lower field (**2a**: 6.74, **2b**: 7.68, **2c**: 6.33 ppm). The $^{31}P$ NMR resonances (**2a**: 25.86, **2b**: 19.12, **2c**: 23.33) are also reflecting the situation of this ring. Obviously, the six-membered chelate ring in **2c** is expanded, which allows the equilibration of the diastereotopic methylene and phenyl protons by either a ring flip of by dissociation/association of the phosphine ligand.

According to the HSAB concept,[17] nickel(II) should - in the given coordination environment - still have the character of a hard Lewis-acid. Accordingly, a series of hard Lewis-bases were reacted with the chloride salt **2aCl** in order to prove whether the coordination of the phosphine donor can be broken. $^{31}P$ NMR spectroscopy clearly shows that the chelate ring of the cation $\mathbf{2a^+}$ does not open even in $CD_3CN$ solution. The same was observed for *tert*-butylisocyanide or carbon monoxide in dichloromethane solution. Several anionic Lewis-bases, such as fluoride, thiocyanide and methanolate were tested in combination with hard and soft cations like $K^+$, $NMe_4^+$ and $NBu_4^+$. None of these experiments resulted in opening the chelate ring. The only reactant that led to ring-opening was cyanide (Scheme 3). To increase its solubility in dichloromethane and its nucleophilicity, the commercially available $NBu_4^+$ salt was applied. An insight into the mechanism in the ring-opening process is given by treatment of **2a($PF_6$)** with $BH_3$ in THF, where again no reactivity was observed. This makes a nucleophilic substitution much more likely than a dissociative process, which should result in the formation of a phosphine-$BH_3$ adduct.




**Scheme 3.** Opening of the P,C-chelate by addition of cyanide; abstraction of the cyanido ligand by gold(I).

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The nickel(II) complex **3** could be recrystallized by slow diffusion of diethyl ether into a solution in dichloromethane giving crystals which were suitable for X-ray structure analysis. Figure 3 shows the solid-state structure of the cation of **3**.

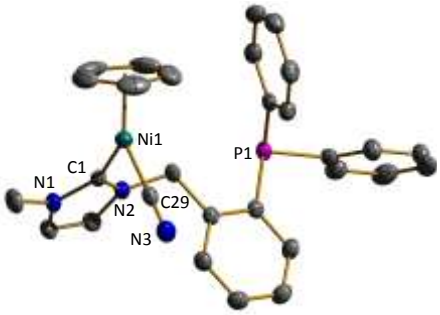


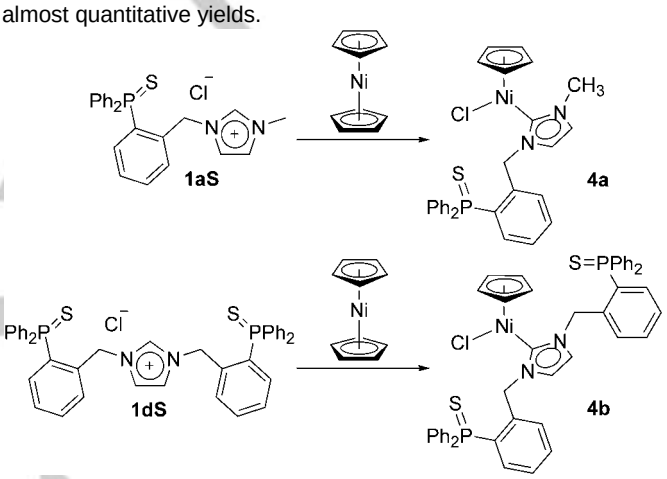

**Figure 3.** Molecular structure of the nickel(II) complex **3** in the solid state. The hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Ellipsoids are at the 50% level. Characteristic bond lengths [Å] and angles [°]: Ni1-C1 1.8773(17), Ni1-$C_{Cp}$ 2.070(2)-2.142(2), Ni1-C29 1.8476(19), N3-C29 1.154(2), C1-Ni1-C29 92.76(7), Ni1-C29-N3 179.27(15).

Although nickel(II)cyanido complexes such as $[Ni(CN)_4]^{2-}$ have been known for long, there are astonishingly little structurally characterized CpNi cyanides in the literature. Butenschön et al. described the synthesis of a nickel(II)cyanido complex bearing an *ansa*-cyclopentadienidephosphine ligand starting from the corresponding chlorido complex by ligand exchange with trimethylsilylcyanide.[18] The bond parameters of compound **3** are completely in agreement with the data reported in their manuscript. In the second CpNi cyanido complex that has been structurally characterized, the cyanido ligand bridges a nickel(II) and a molybdenum(0) center, resulting in largely different structural parameters.[19]

The $^{31}$P NMR spectrum of **3** clearly proves the ring opening due to substitution of the phosphine ligand by cyanide: There is a resonance at -16.04 ppm, typical for the non-coordinated phosphine site. Additionally, there are no longer resonances belonging to diastereotopic methylene protons in the $^{1}$H NMR spectrum and of the diastereotopic phenyl groups in the $^{1}$H and the $^{13}$C NMR spectrum. The $^{13}$C NMR signal of the coordinated cyanido ligand is found at 125.6 ppm, which corroborates bonding to the nickel(II) site via the carbon atom.[18]

Attempts to use the free phosphine site for coordination of a second transition metal failed up to date. When Lewis-acidic metal centers are applied, it seems that abstraction of the cyanido ligand followed by chelating coordination of the phosphine functionalized NHC ligand occurs. Scheme 3 shows exemplarily the outcome of the reaction of compound **3** with (tht)AuCl (tht: tetrahydrothiophene), whereby the color of the reaction mixture turned from red back to green. A $^{31}$P NMR experiment proved that the substrate was completely converted. There are three new signals in the $^{31}$P NMR spectrum: a rather intense one at 25.90 ppm and two weaker at 25.29 und 24.76 ppm, all typical for a nickel(II) coordinated phosphine ligand. In the $^{13}$C NMR spectrum, there is a doublet at 159.1 ppm ($^{2}J_{PC}$ = 37.2 Hz), which data is close to both, the chemical shift and the coupling constant of carbon atom C1 in compound **2a**. The formation of three different aurate(I) anions allows interpretation of the three $^{31}$P NMR resonances, $[Au(CN)Cl]^-$ should be formed as the major product. Findings of Mague support the idea of cyanide abstraction by another metal:[19] He reacted CpNi(CN)($\kappa^1$-dppm) (dppm = bisdiphenylphosphinomethane) with $(C_2H_4)Pt(PPh_3)_2$ and obtained the nickel(I)-platinum(I) complex CpNi-Pt($PPh_3$)(CN)($\kappa^1$,$\kappa^1$-dppm) possessing a Ni-Pt bond and a dppm ligand bridging the two metal sites. The cyanide ligand has shifted to the platinum atom. According to Mague, reacting **2a** with Mo(CO)4(nbd) (nbd = norbornadiene) might result in a bimetallic complex with a bridging cyanido ligand.

By sulfidation of the phosphine site, the formation of open-chained nickel(II) complexes was expected. To achieve this, the imidazolium salts **1aS** and **1dS** were reacted with nickelocene (Scheme 4). The corresponding nickel(II) complexes were formed in almost quantitative yields.




**Scheme 4.** Synthesis of the nickel(II) complexes **4a** and **4d**.

The nickel(II) complexes **4a** and **4d** were recrystallized giving crystals suitable for X-ray structure analysis. Figure 4 shows the solid-state structure of the complexes.

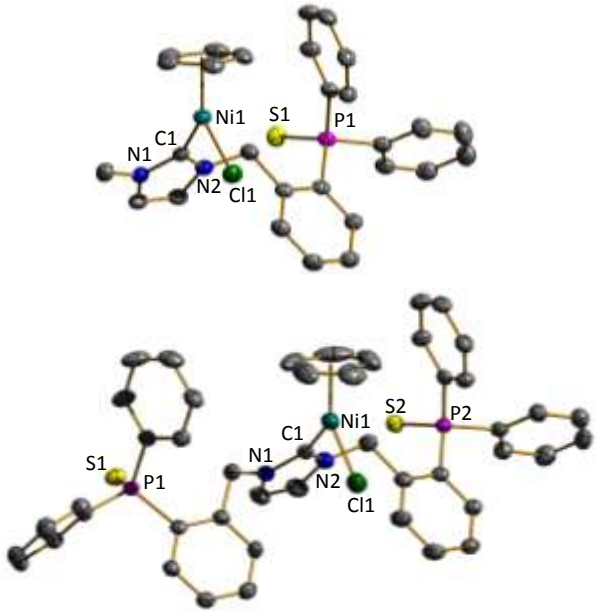



**Figure 4.** Molecular structures of the nickel(II) complex **4a** and **4d** in the solid state. The hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Ellipsoids are at the 50% level. Characteristic bond lengths [Å] and angles [°]: **4a**: Ni1-Cl1 2.1906(6), Ni1-C1 1.8795(18), Ni1-$C_{Cp}$ Ni1-C23 2.065(2)-2.181(2), S1-P1 1.959(1), Cl1-Ni1-C1 93.65(6). **4b**: Ni1-Cl1 2.1865(9), Ni1-C1 1.888(3), Ni1-$C_{Cp}$ 2.082(4)-2.174(4), S1-P1 1.956(1), S2-P2 1.957(1), Cl1-Ni1-C1 93.67(9).

As expected, the bond parameters around the nickel(II) centers are in complete agreement with the complexes described above (Ni-NHC, Ni-Cp) and with the data of other CpNiCl complexes.[16,20] The nickel(II) complex **4d** is rather insoluble in all common solvents. NMR-spectroscopic characterization was only possible in aromatic solvents at elevated temperatures. It's solid state structure shows the formation of chains by strong intermolecular H-π-interactions performed by the $Ph_2PS$ units (see the Supporting Information). In analogy to the cyanidonickel(II) complex **3**, the phosphine moieties in **4a** and **4d** are bent away from the nickel(II) center. However, there is sufficient flexibility in the side chains. Therefore *mer*-chelating coordination to a second metals site seems to be possible for **4d**, allowing for the formation of bimetallic complexes via S,S,Cl-coordination. This will be part of our future investigations in this field.

The chemical shifts of the $^{31}$P NMR signals, which is close to the values found for **1aS** and **1dS**, prove the non-coordinating character of the P=S-units. Except the resonances of the NHC moieties, all other $^{1}$H and $^{13}$C NMR resonances are as expected close those of the imidazolium precursors **1aS** and **1dS**.

## Conclusions

Reacting phosphine functionalized imidazolium chlorides with nickelocene provides the corresponding CpNi-complexes that bear a chelating phosphino-NHC ligand in good yields. The opening of the seven-membered chelate ring occurs via a nucleophilic substitution mechanism and is only possible with strong, hard nucleophiles such as cyanide. Even moderate Lewis acidic molecules such as AuCl are capable to regenerate the chelating binding mode of the P,C-ligand by abstraction of cyanide. With phosphine sulfides instead of phosphine donor sites, the ring closure does not take place. Instead, CpNi chlorido complexes are obtained.

## Experimental Section

**General information:** Commercially available starting materials were obtained from Sigma Aldrich and used without any further purification. Toluene, dichlormethane and diethyl ether were dried in a MB-SPS solvent dryer and acetonitrile was dried over $CaH_2$. The NMR spectra were recorded with r.t. using a Bruker Avance 400 device. Solvent signals were used for the calibration of the spectra. For the assignment of the NMR resonances refer to the Supporting Information, where copies of all relevant NMR spectra can be found. The elemental composition (C,H,N,S) of the products was determined with a vario-micro-cube analyzer (Elementar Analysensysteme GmbH). The infrared spectra were recorded with a Perkin-Elmer FT-IR 1000 spectrometer equipped with a diamond-coated ZnSe-ATR cell. Column chromatography was performed with a Combi Flash Rf200 (Teledyne Isco) chromatograph using packed RediSep® columns. (2-(Chloromethyl)phenyl)diphenylphosphine was synthesized according to ref..[Fehler! Textmarke nicht definiert.] All reactions with nickel(II) compounds were carried out under an atmosphere of nitrogen

**Synthesis of the imidazolium chlorides 1a-d:** One equivalent of 2-(chloromethyl)phenyl)diphenylphosphine and one equivalent of the corresponding imidazole were dissolved in dimethylformamide or acetonitrile and heated to 80 °C for 18 h. After cooling to r.t., the solvent was removed under vacuum. The resulting solid was washed with diethyl ether to remove traces of residual solvent and staring material and dried under vacuum. If necessary, column chromatography (silica, dichloromethane/-methanol) was applied for purification. The strongly hygroscopic chloride salts were stored under an atmosphere of nitrogen.

**1-(2-(Diphenylphosphino)benzyl)-3-methyl-1*H*-imidazol-3-ium chloride (1a)**: 4.00 g of 2-(chloromethyl)phenyl)diphenylphosphine (12.9 mmol), 1.10 g of *N*-methylimidazole (12.2 mmol), 25 mL of acetonitrile, colorless solid (87%). Elemental analysis calcd. for $C_{23}H_{22}ClN_2OP{\cdot}H_2O$ (410.88): C 67.53, H 5.86, N 6.85, found: C 67.23, H 5.89, N, 6.82%. $^{1}$H NMR (400.1 MHz, $CDCl_3$): δ 10.30 (s, 1H, H1), 7.74 (ddd, $^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{PH}$ = 4.5 Hz, $^{4}J_{HH}$ = 1.1 Hz, 1H, H9), 7.44 (td, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{PH}$ = 1.3 Hz, 1H, H8), 7.37 - 7.27 (m, 7H, H7, Ho, Hp), 7.13 (dt, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{PH}$ = 1.3 Hz, 4H, Hm), 7.08, 7.02 (2×dd, $^{3}J_{HH}$ = $^{4}J_{HH}$ =1.1 Hz, 2×1H, H2, H3), 6.95 (ddd, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{PH}$ = 4.4 Hz, $^{4}J_{HH}$ = 1.1 Hz, 1H, H6), 5.74 (s, 2H, H4), 3.89 (s, 2H, $CH_3$). $^{13}$C{1H} NMR (100.6 MHz, $CDCl_3$): δ 138.0 (C1), 137.1 (d, $^{1}J_{PC}$ = 25.8 Hz, Ci), 136.9 (d, $^{1}J_{PC}$ = 15.3 Hz, C10), 134.8 (C7), 134.7 (d, $^{2}J_{PC}$ = 7.9 Hz, C9), 133.8 (d, $^{2}J_{PC}$ = 19.7 Hz, Co), 131.7 (d, $^{2}J_{PC}$ = 4.6 Hz, C5), 130.7, 130.2, 129.5, 122.9 (C2, C3, C6, Cp), 128.9 (d, $^{3}J_{PC}$ = 7.2 Hz), 121.5 (d, $^{3}J_{PC}$ = 4.3 Hz, C8), 51.6 (d, $^{3}J_{PC}$ = 22.6 Hz, C4), 36.5 ($CH_3$). $^{31}$P{1H} NMR (162.0 MHz, $CDCl_3$): δ -17.32 (s). IR (ATR, $cm^{-1}$): 3053w, 2938w, 1571w, 1476w, 1434m, 1320w, 1196w, 1160m, 1112w, 1025w, 830w, 744s, 696s, 675m, 658m.

**1-(2-(Diphenylphosphino)benzyl)-3-(tert-butyl)-1*H*-imidazol-3-ium chloride (1b)**: 3.00 g of 2-(chloromethyl)phenyl)diphenylphosphine (9.65

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mmol), 15 mL DMF, CG with 8.1% of methanol in dichloromethane, colorless solid (76%). Elemental analysis calcd. for $C_{26}H_{28}N_2PCl$ (434.94): C 71.80, H 6.49, N 6.44, found: C 71.52, H 6.46, N 6.29%. $^1$H NMR (400.1 MHz, $CDCl_3$): δ 10.94 (s, 1H, H2), 7.99 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{PH}$ = 4.4 Hz, 1H, H9), 7.42 (td, $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = 1.3 Hz, 1H, H8), 7.37-7.28 (m, 7H, H7, Ho, Hp), 7.21 (s, 1H, H3), 7.19-7.12 (m, 5H, H2, Hm), 6.94 (dd, $^3J_{HH}$ = 6.8 Hz, $^4J_{PH}$ = 4.1 Hz, 1H, H6), 5.90 (s, 2H, H4), 1.62 (s, 9H, H12). $^{13}$C{1H} NMR (100.6 MHz, $CDCl_3$): δ 138.0 (d, $^1J_{PC}$ = 25.9 Hz, Ci), 136.7 (C1), 136.5 (d, $^1J_{PC}$ = 14.4 Hz, C10), 134.8 (d, $^2J_{PC}$ = 7.8 Hz, C9), 134.5 (C7), 133.8 (d, $^2J_{PC}$ = 19.5 Hz, Co), 132.2 (d, $^2J_{PC}$ = 4.4 Hz, C5), 130.6, 130.0, 129.4, 118.7 (C2, C3, C6, Cp), 129.0 (d, $^3J_{PC}$ = 7.1 Hz, Cm), 121.9 (d, $^3J_{PC}$ = 7.2 Hz, C8), 60.4 (C11), 51.1 (d, $^3J_{PC}$ = 21.9 Hz, C4), 30.1 (C12). $^{31}$P{1H} NMR (162.0 MHz, $CDCl_3$): δ -16.51 (s). IR (ATR, cm$^{-1}$): 3058m, 1964w, 1552m, 1478m, 1443m, 1431m, 1376m, 1307m, 1209s, 1136s, 1119m, 996m, 817m, 740s, 961s, 650s.

**1-(2-(Diphenylphosphino)benzyl)-3-mesityl-1*H*-imidazol-3-ium chloride (1c)**: 2.50 g of 2-(chloromethyl)phenyl)diphenylphosphine (8.04 mmol), 1.50 g of *N*-mesitylimidazole (8.05 mmol), 20 mL of acetonitrile, CG with 7.3% of methanol in dichloromethane, colorless solid (81%). Elemental analysis calcd. for $C_{31}H_{30}N_2PCl{\cdot}0.5\ H_2O$ (506.02): C 73.58, H 6.17, N 5.54, found: C 74.07, 6.12, N 5.22%. $^1$H NMR (400.1 MHz, $CDCl_3$): δ 10.68 (s, 1H, H1), 8.02 (ddd, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 4.5 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, H9), 7.54 (br, 1H, H2), 7.40 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{PH}$ = 1.3 Hz, 1H, H8), 7.35-7.24 (m, 7H, H7, Ho, Hp), 7.23-7.17 (m, 4H, Hm), 7.00 (dd, $^3J_{HH}$ = $^4J_{HH}$ =1.1 Hz, 1H, H3), 6.96 (ddd, $^3J_{HH}$ = 7.5 Hz, $^4J_{PH}$ = 4.4 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, H6), 6.93 (s, 2H, Hm'), 2.28 (s, 3H, p'-$CH_3$), 1.97 (s, 6H, o'-$CH_3$). $^{13}$C{1H} NMR (100.6 MHz, $CDCl_3$): δ 141.3 (Ci'), 138.9 (C1), 138.2 (d, $^1J_{PC}$ = 25.6 Hz, Ci), 136.5 (d, $^1J_{PC}$ = 14.1 Hz, C10), 134.9 (d, $^2J_{PC}$ = 7.5 Hz, C9), 134.4 (C7), 134.3 (Co'), 133.9 (d, $^2J_{PC}$ = 19.5 Hz, Co), 131.9 (d, $^2J_{PC}$ = 4.6 Hz, C5), 130.8, 130.7, 129.8, 129.9, 129.5,122.8 (C2, C3, Cm', Cp, Cp', C6), 129.0 (d, $^3J_{PC}$ = 7.2 Hz, Cm), 122.5 (d, $^3J_{PC}$ = 7.9 Hz, C8), 51.1 (d, $^3J_{PC}$ = 21.8 Hz, C4), 21.2 (p'$CH_3$), 17.7 (o'$CH_3$). $^{31}$P{1H} NMR (162.0 MHz, $CDCl_3$): δ -16.05 (s). IR (ATR, cm$^{-1}$): 2959w, 1561w, 1542m, 1478m, 1449m, 1436m, 1368w, 1280m, 1201m, 1194m, 1153m, 1072m, 1015m, 883m, 849m, 782m, 748s, 742s, 727s, 693s, 669m.

**1,3-Bis(2-(diphenylphosphino)benzyl)-1H-imidazol-3-ium chloride (1d):** Method A: 0.45 mL (3.05 mmol) of 1-(trimethylsilyl)-1H-imidazole and 2.00 g (6.44 mmol) 2-(chloromethyl)phenyl)diphenylphosphine were dissolved in 25 mL of toluene. The mixture was heated to reflux for 2d. After cooling to room temperature, the solvent was removed under vacuum and the raw product was purified by chromatography (silica, dichloromethane with 7% of methanol). Colorless solid (59%). Method B: 98.0 mg (1.09 mmol) of sodium imidazolide and 635 mg (2.04 mmol) of 2-(chloromethyl)phenyl)diphenylphosphine were dissolved in 30 mL of acetonitrile and heated to reflux for 2 d. After cooling to room temperature, the solvent was removed under vacuum. The residue was dissolved in 10 mL of dichloromethane, sodium chloride was removed by filtration and the raw product was purified by chromatography (silica, dichloromethane with 7% of methanol). Yield: 63%. Elemental analysis calcd. for $C_{41}H_{35}ClN_2P_2{\cdot}H_2O$ (671.16): C 73.37, H 5.56, N 4.17, found: C 73.19, H 5.52, N4.32%. $^1$H NMR (400.1 MHz, $CDCl_3$): δ 10.73 (s, 1H, H1), 7.78 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{PH}$ = 4.6 Hz, 2H, H9), 7.44 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.1 Hz, 2H, H8), 7.38-7.27 (m, 14H, H7, Ho, Hp), 7.20-7.13 (dt, $^3J_{HH}$ = 8.0 Hz, $^4J_{PH}$ = 1.5 Hz, 8H, Hm), 6.93 (ddd, $^3J_{HH}$ = 7.7 Hz, $^4J_{PH}$ = 4.2 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, H6), 6.88 (s, 2H, H2), 5.63 (s, 4H, H4). $^{13}$C{1H} NMR (100.6 MHz, $CDCl_3$): δ 137.9 (s, C1), 137.2 (d, $^2J_{PC}$ = 25.4 Hz, Ci), 136.6 (d, $^1J_{PC}$ = 14.8 Hz, C10), 134.8 (d, $^2J_{PC}$ = 7.8 Hz, C9), 134.4 (s, C7), 133.9 (d, $^1J_{PC}$ = 19.6 Hz, Co), 131.7 (d, $^2J_{PC}$ = 4.5 Hz, C5), 130.6, 130.0 (2×s, C2, C6), 129.5 (s, Cp), 129.0 (d, $^2J_{PC}$ = 7.3 Hz, Hm), 121.4 (d, $^3J_{PC}$ = 5.2 Hz, C8), 51.2 (d, $^3J_{PC}$ = 22.7 Hz). $^{31}$P{1H} NMR (162.0 MHz, $CDCl_3$): δ -16.35 (s). IR (ATR, cm$^{-1}$): 3049m, 1554m, 1476m, 1433s, 1310w, 1182m, 1147m, 1091m, 1069m, 1026m, 996m, 826w, 742s, 694s, 676m. ESI-MS (m/z): calcd. for [M-Cl]$^+$: 617.23, found: 617.25.

**Synthesis of the phosphine suphides 1aS and 1dS:** One equiv. of sulphur and one equiv. of the corresponding phosphine functionalized imidazolium chloride were dissolved in dichloromethane and heated to reflux for 3 h. After removing the solvent under vacuum, the raw products were purified by column chromatography.

**1-(2-(Diphenylthiophosphino)benzyl)-3-methyl-1*H*-imidazol-3-ium chloride (1aS)**: 2.00 g (5.09 mmol) of **1a**, 177 mg (0.69 mmol) of sulfur, 25 mL of dichlormethane; chromatography (silica, dichlormethane with 14.0% of methanol), colorless solid (84%). Elemental analysis calcd. for $C_{23}H_{22}ClN_2PS{\cdot}H_2O$ (442.94) C 62.37, H 5.46, N 6.32, S 7.24, found: C 62.07, H 5.51, N 6.37, S 7.29%. $^1$H NMR (400.1 MHz, $CDCl_3$): δ 11.03 (s, 1H, H1), 7.82 (t, $^3J_{HH}$ = 2.0 Hz, 1H, H2), 7.79 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{PH}$ = 5.0 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, H6), 7.72 (ddd, $^2J_{PH}$ = 13.7 Hz, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 4H, Ho), 7.62-7.54 (m, 1H, H6, H7), 7.58 (td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 2.1 Hz, 2H, Hp), 7.51 (ddt, $^3J_{HH}$ = 7.6 Hz, $^3J_{PH}$ = 3.2 Hz, $^4J_{HH}$ = 1.5 Hz, 4H, Hm), 7.28 (ddt, $^3J_{HH}$ = 7.8 Hz, $^4J_{PH}$ = 2.1 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H8), 7.06 (t, $^3J_{HH}$ = 1.7 Hz, 1H, H3), 6.91 (ddd, $^2J_{PH}$ = 14.5 Hz, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, H9), 5.74 (s, 2H, H4), 4.02 (s, 3H, $CH_3$). $^{13}$C{1H} NMR (100.6 MHz, $CDCl_3$): δ 138.5 (C1), 136.8 (d, $^2J_{PC}$ = 8.0 Hz, C9), 133.2 (d, $^4J_{PC}$ = 2.7 Hz, C7), 133.0 (d, $^2J_{PC}$ = 7.7 Hz, C5), 133.0 (d, $^3J_{PC}$ = 15.6 Hz, C8), 132.7 (d, $^1J_{PC}$= 88.3 Hz, C10), 132.5 (d, $^4J_{PC}$ = 2.9 Hz, Cp), 132.2 (d, $^2J_{PC}$ = 10.8 Hz, Co), 131.3 (d, $^1J_{PC}$ = 85.2 Hz, Ci), 129.2 (d, $^3J_{PC}$ = 12.8 Hz, Cm), 128.9 (d, $^3J_{PC}$ = 13.3 Hz, C6), 122.8, 122.7 (2×s, C2, C3), 49.6 (d, $^3J_{PC}$ = 6.6 Hz), 36.6 (s, $CH_3$). $^{31}$P{1H} NMR (162.0 MHz, CDCl3): δ 41.71 (s). IR (KBr, cm$^{-1}$): 3147w, 3061m, 2987w, 1627m, 1572m, 1479m, 1437s, 1311m, 1203m, 1159s, 1099s, 1069m, 999m, 832m, 755s, 717s, 696s, 638s, 614s, 523s, 513s, 493m, 467m. ESI-MS (m/z): calcd. for [M-Cl]$^+$: 389.12, found: 389.14.

**1,3-Bis(2-(diphenylthiophosphino)benzyl)-1H-imidazol-3-ium chloride (1dS):** 367 mg (0.56 mmol) of **1d**, 39.5 mg (0.15 mmol) of sulfur, 25 mL of dichlormethane, chromatography (silica, dichlormethane with 10.0% of methanol), colorless solid (80%). Elemental analysis calcd. for $C_{41}H_{35}ClN_2P_2S_2{\cdot}(H_2O)_2$ (753.29): C 65.37, H 5.22, N 3.72, S 8.51, found: C 65.70, H 5.31, N 3.84, S 8.63%. $^1$H NMR (400.1 MHz, $CDCl_3$): δ 11.00 (s, 1H, H1), 7.76 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 4.9 Hz, 2H, H6), 7.68 (ddd, $^2J_{PH}$ = 13.6, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.5 Hz, 8H, Ho), 7.55 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.9 Hz, 4H, Hp), 7.58-7.51 (m, 2H, H7), 7.49 (s, 2H, H2), 7.47 (tdd, $^3J_{HH}$ = 8.4 Hz, $^3J_{PH}$ = 3.1 Hz, $^4J_{HH}$ = 1.3 Hz, 8H, Hm), 7.28 (dt, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H8), 6.88 (ddd, $^3J_{PH}$ = 14.5 Hz, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, H9), 5.69 (s, 4H, H4). $^{13}$C{1H} NMR (100.6 MHz, $CDCl_3$): δ 138.2 (s, C1), 136.9 (d, $^2J_{PC}$ = 8.0 Hz, C9), 133.2 (d, $^4J_{PC}$ = 1.7 Hz, C7), 133.2 (d, $^2J_{PC}$ = 8.7 Hz, C5), 132.9 (d, $^3J_{PC}$ = 10.8 Hz, C8), 132.6 (d, $^1J_{PC}$ = 81.9 Hz, C10), 132.5 (d, $^4J_{PC}$ = 2.9 Hz, Cp), 132.3 (d, $^2J_{PC}$ = 10.9 Hz, Co), 131.4 (d, $^1J_{PC}$ = 85.1 Hz, Ci), 129.1 (d, $^3J_{PC}$ = 12.7 Hz, Cm), 128.9 (d, $^3J_{PC}$ = 11.9 Hz, C6), 122.2 (s, C2), 49.6 (d, $^3J_{PC}$ = 6.6 Hz). $^{31}$P{1H} NMR (162.0 MHz, $CDCl_3$): δ 41.68 (s). IR (KBr, cm$^{-1}$): 3134w, 3056m, 2988w, 1624m, 1556m, 1479m, 1437s, 1311m, 1203m, 1151s, 1100s, 1071m, 997m, 833m, 753s, 713s, 694s, 638s, 614s, 522s, 506s, 495m, 449m. ESI-MS (m/z): calcd. for [M-Cl]$^+$: 681.17, found: 681.18.

**Synthesis of the nickel(II) complexes 2a-c:** One equivalent of nickelocene and one equivalent of the corresponding imidazolium chloride were dissolved in tetrahydrofuran under an atmosphere of nitrogen. The mixture was heated to reflux for 48 h. During this time the chloride complexes **2a-cCl** precipitated as green solids, which were separated from the reaction mixture by filtration. After drying under vacuum, the solid was dissolved in dichloromethane and stirred for 24 h at room temperature with two equivalents of $KPF_6$. The resulting suspension was filtered over Celite® to remove the potassium salts. After removing the solvent under vacuum, the

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resulting green solid was recrystallized by slow diffusion of diethyl ether into a concentrated solution of the compound in dichloromethane.

**(η⁵-Cyclopentadienido)[1-(2-(diphenylphosphino)benzyl)-3-methyl-2*H*-imidazol-2-ylidene]nickel(II) hexafluorophosphate (2a):** 208 mg (0.53 mmol) of **1a**, 100 mg (0.53 mmol) of nickelocene, 30 mL of tetrahydrofuran, 10 mL of dichloromethane and 195 mg (1.06 mmol) of $KPF_6$, green solid (88%). Elemental analysis calcd. for $C_{28}H_{26}F_6N_2NiP_2$ (625.18): C 53.79, H 4.19, N 4.48, found: C 53.80, H 4.34, N 4.51%. $^1$H NMR (400.1 MHz, $CDCl_3$): δ 8.19 (dd, $^3J_{HH}$ = $^3J_{PH}$ = 5.9 Hz, 1H, H9), 8.05 (d, $^3J_{HH}$ = 1.8 Hz, 1H, H2/3), 7.56 (t, $^3J_{HH}$ = 7.6 Hz, 1H, H8), 7.46-7.27 (m, 8H, H7, Ho, Ho', Hm', Hp'), 7.23 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Hp), 7.09 (ddd, $^3J_{HH}$ = 8.3 Hz, $^4J_{PH}$ = 11.4 Hz, $^4J_{PH}$ = 1.7 Hz, 2H, Hm), 6.82 (ddd, $^3J_{HH}$ = 7.9 Hz, $^4J_{PH}$ = 12.1 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H6), 6.79 (d, $^3J_{HH}$ = 1.8 Hz, 1H, H2/3), 6.74, 6.09 (2×d, $^2J_{HH}$ = 14.7 Hz, 2×1H, H4, H4'), 5.39 (s, 5H, CpH), 3.14 (s, 3H, $CH_3$). $^{13}$C{1H} NMR (100.6 MHz, $CDCl_3$): δ 157.3 (d, $^2J_{PC}$ = 38.6 Hz, C1), 141.9 (d, $^2J_{PC}$ = 12.0 Hz, C9), 136.2 (s, C7), 135.3 (d, $^1J_{PC}$ = 46.7 Hz, Ci), 132.5 (d, $^2J_{PC}$ = 8.9 Hz, C5), 132.9 (d, $^4J_{PC}$ = 2.4 Hz, Cp), 132.2 (d, $^1J_{PC}$ = 43.2 Hz, Ci'), 132.2 (d, $^2J_{PC}$ = 11.4 Hz, Co), 131.6 (d, $^2J_{PC}$ = 11.4 Hz, Co'), 131.4 (s, C8), 131.1 (d, $^4J_{PC}$ = 2.6 Hz, Cp'),129.2 (d, $^3J_{PC}$ = 10.6 Hz, Cm), 128.9 (d, $^3J_{PC}$ = 10.7 Hz, Cm'), 128.9 (s, C6), 125.7, 125.4 (2×s, C2, C3), 125.5 (d, $J_{PC}$ = 47.7 Hz, C10), 93.0 (s, CpC), 53.5 (d, $^3J_{PC}$ = 5.4 Hz, C4), 37.6 ($CH_3$). $^{31}$P{1H} NMR (162.0 MHz, $CDCl_3$): δ 25.86 (s), -144.25 (hept, $^1J_{PF}$ = 713.0 Hz). $^{19}$F{1H} NMR (376.5 MHz, $CDCl_3$): δ -73.06 (d, $^1J_{PF}$ = 712.5 Hz). IR (ATR, cm$^{-1}$): 3143w, 2353w, 1568w, 1482m, 1461m, 1436m, 1404m, 1356m, 1289w, 1233m, 1182m, 1098m, 1054w, 923w, 878m, 825s, 747s, 724s, 711m, 695s, 685s.

**(η⁵-Cyclopentadienido)[1-(2-(diphenylphosphino)benzyl)-3-tert-butyl-2*H*-imidazol-2-ylidene]nickel(II) hexafluorophosphate (2b):** 200 mg (0.46 mmol) of **1b**, 87 mg (0.46 mmol) of nickelocene, 25 mL of tetrahydrofuran, 10 mL of dichloromethane and 169 mg (0.92 mmol) of $KPF_6$, green solid (67%). Elemental analysis calcd. for $C_{31}H_{32}F_6N_2NiP_2$ (667.26): C 55.80, H 4.83, N 4.20, found: C 55.71, H 4.97, N 4.23%. $^1$H NMR (400.1 MHz, $CD_2Cl_2$): δ 7.69-7.66 (m, 1H, H9), 7.68 (d, $^2J_{HH}$ = 14.9 Hz, 1H, H4), 7.57 (tt, $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = $^4J_{HH}$ = 1.3 Hz, 1H, H8), 7.54-7.42 (m, 8H, H7, Ho, Ho', Hm', Hp'), 7.35 (d, $^3J_{HH}$ = 2.1 Hz, 1H, H2/3), 7.29 (t, $^3J_{HH}$ = 7.7 Hz, 1H, Hp), 7.15 (ddd, $^3J_{HH}$ = 7.0 Hz, $^4J_{PH}$ = 11.5 Hz, $^4J_{PH}$ = 1.6 Hz, 2H, Hm), 7.04, (d, $^3J_{HH}$ = 2.1 Hz, 1H, H2/3), 6.95 (ddd, $^3J_{HH}$ = 7.9 Hz, $^4J_{PH}$ = 10.9 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, H6), 5.37 (s, 5H, CpH), 5.16 (d, $^2J_{HH}$ = 14.9 Hz, 1H, H4'), 1.20 (s, 9H, H12). $^{13}$C{1H} NMR (100.6 MHz, $CD_2Cl_2$): δ 152.0 (d, $^2J_{PC}$ = 33.0 Hz, C1), 142.1 (d, $^2J_{PC}$ = 12.8 Hz, C9), 137.6 (s, C7), 136.2 (d, $^1J_{PC}$ = 46.7 Hz, Ci), 133.1 (d, $^4J_{PC}$ = 2.3 Hz, Cp), 133.0 (d, $^2J_{PC}$ = 10.6 Hz, Co), 131.8 (d, $^2J_{PC}$ = 11.0 Hz, Co'), 131.2 (d, $^2J_{PC}$ = 9.1 Hz, C5), 131.2 (s, C8), 130.9 (d, $^1J_{PC}$ = 46.2 Hz, Ci'), 131.6 (d, $^4J_{PC}$ = 2.6 Hz, Cp'),129.9 (s, C6), 129.8 (d, $^3J_{PC}$ = 10.4 Hz, Cm), 129.6 (d, $^3J_{PC}$ = 10.6 Hz, Cm'), 127.3 (d, $J_{PC}$ = 46.7 Hz, C10), 124.3, 123.3 (2×s, C2, C3), 95.9 (s, CpC), 59.2 (s, C11), 55.6 (d, $^3J_{PC}$ = 7.2 Hz, C4), 31.2 (C12). $^{31}$P{1H} NMR (162.0 MHz, $CD_2Cl_2$): δ 19.12 (s), -144.43 (hept, $^1J_{PF}$ = 710.6 Hz). $^{19}$F{1H} NMR (376.5 MHz, $CD_2Cl_2$): δ -73.17 (d, $^1J_{FP}$ = 710.7 Hz). IR (ATR, cm$^{-1}$): 2983w, 1923w, 1549m, 1479m, 1447m, 1435m, 1379m, 1310m, 1237m, 1191m, 1118m, 1094m, 876m, 828s, 744s, 694s, 655m.

**(η⁵-Cyclopentadienido)[1-(2-(diphenylphosphino)benzyl)-3-mesityl-2*H*-imidazol-2-ylidene]nickel(II) hexafluorophosphate (2c):** 200 mg (0.40 mmol) of **1c**, 76 mg (0.40 mmol) of nickelocene, 25 mL of tetrahydrofuran, 10 mL of dichloromethane and 148 mg (0.80 mmol) of $KPF_6$, green solid (92%). Elemental analysis calcd. for $C_{36}H_{33}F_6NiN_2P_2{\cdot}CH_2Cl_2$ (813.25): C 54.65, H 4.34, N 3.44, found: C 54.41, H 4.44, N 3.54%. $^1$H NMR (400.1 MHz, $CDCl_3$): δ 7.75-7.68 (m, 1H, H9), 7.72 (d, $^3J_{HH}$ = 1.8 Hz, 1H, H2/3), 7.67-7.33(m, 11H, H7, H8, Ho, Ho', Hm', Hm'', Hp'), 7.29 (t, $^3J_{HH}$ = 7.9 Hz, 1H, Hp), 7.21 (ddd, $^3J_{HH}$ = 8.3 Hz, $^4J_{PH}$ = 11.4 Hz, $^4J_{PH}$ = 1.7 Hz, 1H, Hm), 7.00 (br, 2H, H6, Hm'), 6.79 (d, $^3J_{HH}$ = 1.9 Hz, 1H, H2/3), 6.33, 5.24 (2×dbr, $^2J_{HH}$ = 10.5 Hz, 2×1H, H4, H4'), 4.74 (s, 5H, CpH), 2.36 (s, 3H, p''-$CH_3$), 1.93, 1.64 (2×br, 2×3H, 2×o''-$CH_3$). $^{13}$C{1H} NMR (100.6 MHz, $CDCl_3$): δ 160.9 (d, $^2J_{PC}$ = 24.9 Hz, C1), 142.2 (d, $^2J_{PC}$ = 12.6 Hz, C9), 140.2 (s, Ci''), 136.2 (s, C7), 135.2 (br, Ci), n.b. (Ci'), 132.6 (d, $^2J_{PC}$ = 11.6 Hz, Co), 133.3 (s, Co''), 132.6 (d, $^2J_{PC}$ = 22.0 Hz, C5), 131.4 (br, Co', Cp, Cp', C8), 131.3 (d, $^3J_{PC}$ = 8.0 Hz, Cm''), 132.6 (s, Cp''),129.5 (d, $^3J_{PC}$ = 7.2 Hz, Cm), 129.5 (br, Cm', C6), 128.1 (d, $J_{PC}$ = 43.5 Hz, C10), 126.2, 124.8 (2×s, C2, C3), 94.5 (CpC), 54.1 (d, $^3J_{PC}$ = 10.7 Hz, C4), 21.2 (p''-$CH_3$), 17.9 (o''-$CH_3$). $^{31}$P{1H} NMR (162.0 MHz, $CDCl_3$): δ 23.33 (s), -144.17 (hept, $^1J_{PF}$ = 712.8 Hz). $^{19}$F{1H} NMR (376.5 MHz, $CDCl_3$): δ -72.90 (hept, $^1J_{PF}$ = 712.7 Hz). IR (ATR, cm$^{-1}$): 3148w, 2968w, 1612w, 1569w, 1480m, 1437m, 1410m, 1281m, 1238m, 1114w, 1089m, 1021w, 935w, 877m, 829s, 792s, 747s, 692s.

**(Cyanido)(η⁵-cyclopentadienido)[1-(2-(diphenylphosphino)benzyl)-3-methyl-2*H*-imidazol-2-ylidene]nickel(II) (3):** 467 mg (0.91 mmol) of the nickel(II) complex **2a** (used without further purification) and 272 mg (0.96 mmol) of tetra(n-butyl)ammonium cyanide were dissolved in 40 mL of dichloromethane. The mixture was heated to reflux for 16 h. After removing the solvent, the product was purified by column chromatography (silica, dichloromethane with 5% of methanol). It was recrystallized by slow diffusion of diethyl ether into a dichloromethane solution. Red crystals (79%). Elemental analysis calcd. for $C_{29}H_{26}N_3NiP{\cdot}CH_2Cl_2$ (591.16): C 60.95, H 4.77, N 7.11, found: C 60.74, H 4.94, N 7.02%. $^1$H NMR (400.1 MHz, $CDCl_3$): δ 7.42-7.37 (m, 6H, Ho, Hp), 7.35-7.28 (m, 5H, Hm, H9), 7.22 (td, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H8), 6.99-6.94 (m, 2H, H6, H7), 6.88, 6.77 (2×d, $^3J_{HH}$ = 2.0 Hz, 2H, H3), 5.77 (br, 2H, H4), 5.14 (s, 5H, CpH), 4.01 (s, 3H, $CH_3$) ppm. $^{13}$C{1H} NMR (100.6 MHz, $CDCl_3$): δ 167.1 (C1), 140.0 (d, $^1J_{PC}$ = 23.1 Hz, Ci), 135.8 (d, $J_{PC}$ = 15.3 Hz, C10), 135.3 (d, $^2J_{PC}$ = 9.0 Hz, C5), 134.2 (d, $^2J_{PC}$ = 19.9 Hz, Co), 133.5 (s, C7), 129.6, 128.3 (2×s, C6, C8), 129.4 (s, Cp), 128.9 (d, $^3J_{PC}$ = 7.2 Hz, Cm), 128.1 (d, $^2J_{PC}$ = 4.6 Hz, C9), 125.6 (s, CN), 124.0, 122.5 (2s, C2, C3), 90.9 (s, CpC), 53.1 (d, $J_{PC}$ = 28.0 Hz, C4), 38.9 (s, $CH_3$). $^{31}$P{1H} NMR (162.0 MHz, $CDCl_3$): -16.04. IR (ATR, cm$^{-1}$): 3163w, 3131w, 3104w, 3054w, 3012w, 2938w, 2109s, 1587w, 1568w, 1455m, 1432s, 1352m, 1310w, 1236s, 1198m, 1090m, 1068m, 996m, 979m, 837w, 795s, 752s, 744s, 728s, 796s, 669m.

**Synthesis of the nickel(II) complexes 4a and 4d:** One equivalent of the sulfidated imidazolium salt and one equivalent of nickelocene were dissolved in tetrahydrofuran and heated to reflux for 18 h under an atmosphere of nitrogen. After cooling to room temperature, the red suspension was filtered. The solvent was removed from the filtrate under vacuum, the solids were washed with diethyl ether.

**Chlorido(η⁵-cyclopentadienido)[1-(2-(diphenylphosphino)benzyl)-3-methyl-2*H*-imidazol-2-ylidene]nickel(II) (4a):** 202 mg (0.48 mmol) of **1aS**, 91.0 mg (0.48 mmol) of nickelocene, 40 mL of tetrahydrofuran. Recrystallization by slow diffusion of diethyl ether into a dichloromethane solution, red crystals (97%). Elemental analysis calcd. for $C_{28}H_{26}ClN_2NiPS{\cdot}(CH_2Cl_2)_{0.1}$ (556.22): C 60.68, H 4.75, N 5.04, S 5.76, found: C 60.56, H 4.94, N 5.07, S 5.89. $^1$H NMR (400.1 MHz, $CDCl_3$): δ 7.86 (br, 4H, Ho), 7.55 (br, 4H, Hm), 7.42 (br, 3H, Hp, H9), 7.29-7.07 (m, 1H, H8), 7.01-6.75 (m, 4H, H2, H3, H6, H7), 5.22 (br, 2H, H4), 4.95 (br, 5H, CpH), 4.30 (s, 3H, $CH_3$) broad resonances probably due to paramagnetic impurities. $^{13}$C{1H} NMR (100.6 MHz, $CDCl_3$): δ 161.3 (C1), 140.5 (d, $^2J_{PC}$ = 8.1 Hz, C9), 133.0-122.0 div. overlapping signals, 131.5 (d, $^3J_{PC}$ = 9.1 Hz, C8), 129.1 (d, $^3J_{PC}$ = 12.3 Hz, Cm), 127.6 (d, $^3J_{PC}$ =12.3 Hz, C6), 124.1, 122.6 (2×s, C2, C3), 91.7 (CpC), 52.7 (d, $^3J_{PC}$ = 6.3 Hz, C4), 38.9 ($CH_3$). $^{31}$P{1H} NMR (162.0 MHz, $CDCl_3$): δ 41.69 (s). IR (KBr, cm$^{-1}$): 3157w, 3124m, 3101w, 3045w, 2918w, 1624w, 1589m, 1569m, 1478m, 1470m, 1435s, 1409s, 1343m, 1310m, 1237s, 1211m, 1096s, 1070m, 997m, 834m, 790s, 753s, 737s, 723s, 712s, 695s, 638s, 614m, 522s, 496m, 450m. ESI-MS (m/z): $[M\text{-}Cl]^+$ calcd: 511.09, found: 511.13, $[M\text{-}C_5H_4NiCl]^+$ calcd: 389.12, found: 389.14.

**Chlorido(η$^5$-cyclopentadienido)[1,3-bis(2-(diphenylthiophosphino)-benzyl)-2*H*-imidazol-2-ylidene]nickel(II) (4d):** 156 mg (0.22 mmol) of **1dS**, 43.0 mg (0.23 mmol) of nickelocene, 40 mL of tetrahydrofuran. Recrystallization from toluene, red crystals (82%). Elemental analysis calcd. for $C_{46}H_{39}ClN_2NiP_2S_2\cdot(C_7H_8)_{0.5}$ (886.13): C 67.09, H 4.89, N 3.16, S 7.24, found: C 67.00, H, 4.99, N 3.11, S 7.01%. $^1$H NMR (600.1 MHz, $C_6D_6$, 70 °C): δ 7.98 (ddd, 8H, $^2J_{PH}$ = 13.4 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 3.2 Hz, Ho), 7.94 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{PH}$ = 5.1 Hz, H6), 7.15-7.10 (m, 14H, Hm, Hp, H7), 7.03 (dd, $^3J_{PH}$ = 14.5 Hz, $^3J_{HH}$ = 7.7 Hz, 2H, H9), 6.79 (t, $^3J_{HH}$ = 7.7 Hz, 2H, H8), 6.77 (s, 2H, H2), 6.63 (br, 4H, H4), 4.79 (s, 5H, CpH). $^{13}$C{1H} NMR (150.9 MHz, $C_6D_6$, 70 °C): δ 165.8 (C1), 141.7 (d, $^2J_{PC}$ = 7.9 Hz, C9), 133.9 (d $^1J_{PC}$ = 86.0 Hz, C10), 133.4 (d, $^1J_{PC}$ = 83.4 Hz, Ci), 132.9 (d, $^2J_{PC}$ = 10.6 Hz, Co), 132.6 (d, $^4J_{PC}$ = 2.4 Hz, C7), 132.3 (d, $^2J_{PC}$ = 9.3 Hz, C5), 132.2 (d, $^3J_{PC}$ = 10.9 Hz, C8), 131.8 (d, $^4J_{PC}$ = 2.5 Hz, Cp), 129.0 (d, $^3J_{PC}$ = 12.4 Hz, Cm), 127.5 (d, $^3J_{PC}$ = 12.2 Hz, C6), 123.3 (C2), 92.0 (CpC), 53.5 (d, $^3J_{PC}$ = 6.8 Hz). $^{31}$P{1H} NMR (243.0 MHz, $C_6D_6$, 70 °C): δ 41.41 (s). IR (KBr, cm$^{-1}$): 3163w, 3130w, 3057m, 2968w, 2918w, 1615w, 1590m, 1572w, 1480m, 1436s, 1409s, 1361m, 1310m, 1234s, 1177m, 1129m, 1100s, 1069m, 1027m, 998m, 384w, 779m, 752s, 714s, 696s, 639s, 614m, 517s, 498m, 450m. ESI-MS (m/z): [M-Cl]$^+$ calcd: 803.14, found: 803.20.

### X-ray structure analyses

X-ray structure analyses: Crystal data and refinement parameters for compounds **1a**, **1d**, **2a-2c**, **3**, **4a** and **4d** are collected in Table 2. All structures were solved using direct methods (SIR92 [21]), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures.[22] Analytical numeric absorption corrections were applied on complexes **3** and **4d**, for the other compounds semi-empirical absorption corrections from equivalents (Multiscan) were carried out.[23] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined by using a riding model. In the structure of complex **2c**, because of the existence of severely disordered / partially occupied $Et_2O$, SQUEEZE process integrated in PLATON [24] was used. And the detailed information has been posted in the final CIF file. CCDC 1837457 - 1837464 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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**Table 2.** Crystallographic data, data collection and refinement.

| | **1a** | **1d** | **2a** | **2b** | **2c** | **3** | **4a** | **4d** |
|---|---|---|---|---|---|---|---|---|
| empirical formula | $C_{23}H_{22}F_6N_2P_2$ | $C_{44}H_{41}ClN_2OP_2$ | $C_{28}H_{26}F_6N_2NiP_2$ | $C_{31}H_{32}F_6N_2NiP_2$ | $C_{36}H_{34}F_6N_2NiP_2$ | $C_{30}H_{28}Cl_2N_3NiP$ | $C_{28}H_{26}ClN_2NiPS$ | $C_{63.50}H_{59}ClN_2NiP_2S_2$ |
| formula weight | 502.37 | 711.18 | 625.16 | 667.23 | 729.30 | 591.13 | 547.70 | 1070.34 |
| crystal size [mm] | 0.37x0.14x0.10 | 0.23x0.12x0.12 | 0.39x0.30x0.24 | 0.44x0.30x0.28 | 0.61x0.24x0.23 | 0.48x0.17x0.15 | 0.31x0.24x0.16 | 0.52x0.07x0.05 |
| $T$ [K] | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) |
| $\lambda$ [Å] | 1.54184 | 1.54184 | 1.54184 | 1.54184 | 1.54184 | 1.54184 | 1.54184 | 1.54184 |
| crystal system | monoclinic | triclinic | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ | P-1 | $P2_1/c$ | $P2_1/c$ | C2/c | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ |
| $a$ [Å] | 7.4335(2) | 9.2271(3) | 8.9868(1) | 20.1470(3) | 26.4688(3) | 9.0289(1) | 8.8039(1) | 8.6986(2) |
| $b$ [Å] | 10.9520(3) | 14.6943(8) | 21.9337(3) | 8.9594(1) | 9.0123(1) | 18.4406(2) | 17.1760(3) | 25.6648(6) |
| $c$ [Å] | 28.1889(7) | 14.8473(6) | 13.5453(1) | 17.7413(3) | 30.1964(4) | 16.9566(2) | 17.2485(3) | 24.6486(6) |
| $\alpha$ [°] | 90 | 92.748(4) | 90 | 90 | 90 | 90 | 90 | 90 |
| $\beta$ [°] | 95.579(2) | 98.994(3) | 93.170(1) | 111.885(2) | 100.698(1) | 102.281(1) | 96.387(2) | 97.375(2) |
| $\gamma$ [°] | 90 | 104.917(4) | 90 | 90 | 90 | 90 | 90 | 90 |
| $V$ [Å$^3$] | 2284.04(10) | 1913.10(14) | 2665.88(5) | 2971.61(8) | 7078.00(15) | 2758.64(5) | 2592.06(7) | 5457.2(2) |
| $Z$ | 4 | 2 | 4 | 4 | 8 | 4 | 4 | 4 |
| $\rho_{calcd.}$ [g cm$^{-3}$] | 1.461 | 1.235 | 1.558 | 1.491 | 1.369 | 1.423 | 1.403 | 1.303 |
| $\mu$ [mm$^{-1}$] | 2.308 | 1.948 | 2.759 | 2.512 | 2.160 | 3.531 | 3.508 | 2.550 |
| $\theta$-range [°] | 3.15-62.78 | 3.13-62.75 | 3.840-62.695 | 4.731-62.705 | 4.083-62.706 | 3.586-62.729 | 3.643-62.684 | 3.444-62.685 |
| refl. coll. | 14918 | 12693 | 19391 | 21059 | 13496 | 19270 | 9823 | 24119 |
| indep. refl. | 3670 [$R_{int}$ = 0.0311] | 6089 [$R_{int}$ = 0.0238] | 4270 [$R_{int}$ = 0.0251] | 4733 [$R_{int}$ = 0.0317] | 5649 [$R_{int}$ = 0.0182] | 4407 [$R_{int}$ = 0.0240] | 4135 [$R_{int}$ = 0.0283] | 8681 [$R_{int}$ = 0.0469] |
| data/restr./param. | 3670/0/300 | 6089/0/453 | 4270/0/353 | 4733/99/413 | 5649/0/427 | 4407/0/335 | 4135/0/308 | 8681/378/744 |
| final $R$ indices [$I>2\sigma(I)$] [a] | 0.0379, 0.0955 | 0.0660, 0.1964 | 0.0329, 0.0837 | 0.0366, 0.0946 | 0.0368, 0.0939 | 0.0266, 0.0676 | 0.0303, 0.0693 | 0.0468, 0.1041 |
| $R$ ind. (all data) | 0.0431, 0.0998 | 0.0702, 0.2021 | 0.0346, 0.0852 | 0.0387, 0.0966 | 0.0387, 0.0970 | 0.0281, 0.0690 | 0.0353, 0.0728 | 0.0632, 0.1127 |
| *GooF* [b] | 1.050 | 1.052 | 1.053 | 1.078 | 1.058 | 1.033 | 1.048 | 1.044 |
| $\Delta\rho_{max/min}$ (e·Å$^{-3}$) | 0.574/-0.303 | 1.641/-0.577 | 0.709/-0.380 | 0.882/-0.320 | 0.600/-0.469 | 0.305/-0.229 | 0.270/-0.303 | 0.594/-0.358 |

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $\omega R2 = [\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma\omega F_o^2]^{1/2}$. [b] $GooF = [\Sigma\omega(F_o^2 - F_c^2)^2/(n\text{-}p)]^{1/2}$.

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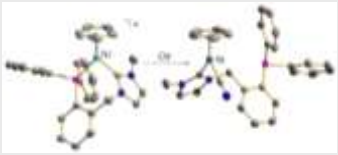

Only cyanide is able to open up the seven-membered phosphine-NHC chelate ring of CpNi complexes.

*Jens Trampert, Marcel Nagel, Tobias Grimm, Yu Sun and Werner R. Thiel**

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**Phosphine functionalized NHC ligands and their cyclopentadienide nickel(II) complexes**

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