Fundamental reactivity of the Metal-Carbon bond in cyclometalated PNC-complexes
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Arene C$_{sp}^{2}$-H Activation at Ni$^{II}$ modeled with Reactive PNC$_{Ph}$ Ligands

4.1 Introduction

C-H activation is enjoying widespread attention as an efficient and selective methodology for the functionalization of hydrocarbons. Cyclometalation typically precedes the functionalization of aryl C$_{sp}^{2}$-H bonds, often using the ligating effect of a neighboring group to orient the C-H bond within the metal coordination sphere. Pyridine has proven very efficient as a directing group, and a variety of second- and third-row metal based systems facilitate the selective C-H functionalization of pyridylarenes. In stark contrast with its second-row congener Pd, Ni-based systems were very underdeveloped for selective C-H functionalization of aromatic substrates until recently.

Scheme 4.1: Well-defined routes A-D toward cyclometalated Ni$^{II}$ species and new direction presented in this Chapter, involving direct cyclometalation of an arene C-H bond.

For stoichiometric cyclometalation at Ni, the Ni-C bond is generally formed via oxidative addition of a carbon-halide (to Ni$^{0}$; Scheme 4.1 A)\textsuperscript{16,22} decarboxylation (B)\textsuperscript{23}.
or transmetallation from a lithiated derivative (C). Formation of a Ni-C bond from an unactivated C-H bond is only common for encumbering ligand structures that enforce the C-H bond in close proximity of the metal, such as the pincer-type ECE ligands and macrocyclic ligand structures (D). For less restricting bidentate ligand structures, procedures involving direct C-H activation pathways with nickel are rare, despite the fact that the first reported cyclometalated complex ever reported involves the reaction of nickelocene with azobenzene.

Although stoichiometric C-H metalation of ligands is uncommon for Ni, the formation of such a nickelacycle was recently postulated as key step in the Ni-catalyzed aromatic C-H bond functionalization, using a bidentate directing-group approach. Despite intermediacy of nickelacycles in various catalytic processes, including ethylene oligo- and polymerization, only few systematic reactivity studies of the Ni-carbon bond in these entities are reported. Furthermore, very little information is available on agostic Ni complexes with a specific Ni-(C-Ar-H) interaction. While this type of bonding most likely precedes the actual C-H activation or metatation step and is therefore an interesting research topic for the fundamental understanding of C-H bond activation processes, isolated complexes with agostic interactions are scarcely documented for first-row TM pincer complexes.

In Chapters 2 and 3 we introduced reversible cyclometalation as strategy for cooperative catalysis, using a strongly chelating P,N-ligand that featured a flanking phenyl arm. Expanding on these results, we set out to investigate the potential for cyclometalation with this tridentate ligand. Ligand 1 is developed as a more robust alternative to ligand that features a reactive linker between the phosphine and pyridine unit and for the difference in electronic character. In this Chapter, we report the facile and selective C-H metalation of ligand 1 and ligand 1 to Ni. Furthermore, the reactivity of the M-C bond with the strong acid HBF₄ is investigated, which resulted in the isolation of complexes with a similar M-(C₆H₅-H) interaction as was reported for Rh (Chapter 2). The nature of this interaction was studied with DFT calculations which show that a weak interaction between the C₆H₅-H and Ni is present that mainly has Ni-(η₁-C₆H₅) character.

### 4.2 Results and Discussion

#### 4.2.1 C-H Activation at Ni

Ligand 1 (see Chapters 2 and 3) can be easily coordinated to NiBr₂(DME) to form the purple paramagnetic complex 2. This complex has an effective magnetic moment μₑffective of 3.01 at 20 °C in acetone as determined by Evans’ method. Suitable crystals for single crystal X-ray diffraction are obtained by layering a CH₂Cl₂ solution with pentane and the crystal structure reveals a pseudo-tetrahedral geometry around the Ni center (Figure 4.1 left), with ζNi-Ni-P1 at 120.07(4)° and ζNi-Ni-Br2 at 121.18(4)°, in accordance with the paramagnetic nature of the complex.

Phosphinite ligand 1 is synthesized by reacting 6-phenyl-2-pyridone and di-tert-butylchlorophosphine mediated by a weak base, NEt₃, to ensure deprotonation of the 2-hydroxypyridine tautomeric form. Upon coordination to NiBr₂(DME), the resulting
Cyclometalation at Ni

brown complex \(2^0\) is obtained, which has an effective magnetic moment \(\mu_{\text{eff}}\) of 3.29 at 20 °C in CH\(_2\)Cl\(_2\). The solid state structure shows a distorted tetrahedral structure due to the flanking Ph ring, with \(\angle\text{Ni}-\text{Ni}-\text{Br1}\) at 95.71(7)° and \(\angle\text{Ni}-\text{Ni}-\text{Br2}\) at 144.27(7)° [Figure 4.1 right]. The reason behind the structural differences in \(2^\text{CH}_2\) and \(2^0\) is unclear. It might be merely a packing effect resulting from different orientation of the Ph-ring.

Figure 4.1: ORTEP (ellipsoids set at 50 % probability) for complex \(2^\text{CH}_2\) (left) and \(2^0\) (right). Selected bond lengths [Å] and angles [°] for \(2^a\): Ni1-P1 2.3095(5); Ni1-N1 2.0512(16); Ni1-Br1 2.4028(3); Ni1-Br2 2.3499(4); P1-Ni1-N1 84.93(4); P1-Ni1-Br1 109.343(17); P1-Ni1-Br2 108.003(17); Ni1-P1-C12 93.66(6); N1-Ni1-Br1 102.07(4); N1-Ni1-Br2 121.18(4); Br1-Ni1-Br2 124.220(14); torsion angle Ni-C5-C15-C16 38.6(2); C1-C6-C7-N1 38.6(2). For \(2^b\): Ni1-P1 2.2859(9); Ni1-N1 2.075(3); Ni1-Br1 2.3535(5); Ni1-Br2 2.3555(5); P1-Ni1-N1 84.93(4); P1-Ni1-Br1 109.343(17); P1-Ni1-Br2 108.003(17); Ni1-P1-C12 93.66(6); N1-Ni1-Br1 102.07(4); N1-Ni1-Br2 121.18(4); Br1-Ni1-Br2 124.220(14); torsion angle Ni-C5-C15-C16 38.6(2); C1-C6-C7-N1 38.6(2). Comparable (N^\(\text{P}\))NiX\(_2\) complexes show less distortion from the tetrahedral geometry and usually give lower values for \(\mu_{\text{eff}}\). The value for \(\mu_{\text{eff}}\) of \(2^\text{CH}_2\) and \(2^0\) corresponds more to the values that were found for bimetallic trigonal bipyramidal structures with bridging chlorides. However, magnetic properties for Ni\(^{n}\) complexes are highly dependent on the ligand field and large deviations can be found due to structural equilibria in solution.

The first attempts of performing C-H activation at the ortho-position of the phenyl group in complex \(2^\text{CH}_2\) were performed in presence of NaOAc. This is the preferred base for C-H activation at other metals, such as Pd, Rh and Ru, because it can deprotonate a
strong C-H bond via the concerted-metalation-deprotonation (CMD) pathway, wherein the C-H bond is coordinating to the metal with an agostic interaction and a favorable six-membered TS can be formed. However, the reaction between Ni-complex $2^{\text{CH}_2}$ and NaOAc in THF always resulted in paramagnetic mixtures with broad peaks in $^1$H NMR, while the cyclometalated product $3^{\text{CH}_2}$ is expected to be diamagnetic due to the anticipated pincer-like coordination, leading to a square planar geometry. This suggests that either the reaction does not go to completion or paramagnetic side products are present.

Figure 4.2: ORTEP (ellipsoids set at 50% probability) for complex $3^{\text{CH}_2}$ (left) and $3^{\text{O}}$ (right). Selected bond lengths [Å] and angles [°] for $3^{\text{CH}_2}$: Ni1-P1 2.253(1); Ni1-N1 1.896(3); Ni1-C1 1.928(4); Ni1-Br1 2.3153(6); P1-Ni1-N1 85.7(1); P1-Ni1-Br1 95.85(3); P1-Ni1-C1 169.8(1); Ni-Ni1-C1 84.1(1); Ni-Ni1-Br1 177.8(1); Ni1-P1-C1 98.4(1); torsion N1-C5-C15-C16 38.6(2); C1-C6-C7-N1 38.6(2). For $3^{\text{O}}$: Ni1-P1 2.2046(11); Ni1-N1 1.875(3); Ni1-C1 1.923(4); Ni1-Br1 2.3023(6); P1-Ni1-N1 82.99(10); P1-Ni1-Br1 97.25(3); P1-Ni1-C1 166.28(12); N1-Ni1-C1 83.91(15); N1-Ni1-Br1 178.58(10).

Many different combinations of bases (KOAc, NEt$_3$, DBU, KOtBu), solvents (THF, toluene, MeCN, dioxane) and temperatures were applied but only the combination of NEt$_3$ in toluene gave the desired reaction. After addition of NEt$_3$ to a suspension of complex $2^{\text{CH}_2}$ or $2^{\text{O}}$ in toluene at 50 °C, the color of the solution changed to yellow in 30-60 minutes and the NEt$_3$·HCl salt was formed as a white precipitate (Scheme 4.2). Diamagnetic products $3^{\text{CH}_2}$ and $3^{\text{O}}$ were obtained that show well-defined NMR spectra, with seven distinct aromatic signals in $^1$H NMR and a singlet in $^{31}$P NMR (45.53 ppm and 187.05 ppm, respectively) suggesting a carbon atom bound to the Ni-center in trans position of the phosphine. Crystals suitable for X-ray analysis could be grown from THF/pentane mixtures and the molecular structures of $3^{\text{CH}_2}$ and $3^{\text{O}}$ confirm the cyclometalation (Figure 4.2). The structures show a slightly distorted square planar geometry around the nickel center (φ P1-Ni1-C1 at 169.8(1)° ($3^{\text{CH}_2}$) and 166.28(12)° ($3^{\text{O}}$)). The Ni1-C1 bond lengths (1.928(4) Å for $3^{\text{CH}_2}$ and 1.923(4) Å for $3^{\text{O}}$) are similar to that observed for the other ‘unforced’ nickelacycles discussed in the

\[\text{The large downfield} \quad ^{31}\text{P NMR shift of} \quad 3^{\text{O}} \quad \text{is due to the higher electronegativity of the oxygen linker connected to phosphorus}\]
introduction, which all fall in the range of 1.91-1.95 Å.

Why the combination of NEt$_3$ and toluene works so well is unclear at the moment. The reason could be related to the insolubility of the NEt$_3$-HCl salt in toluene, although the reaction in NEt$_3$/THF produced a paramagnetic mixture while the NEt$_3$-HCl salt is not soluble in THF either. However, after we discovered the specific combination of NEt$_3$/toluene, we found more examples in literature that use this combination for stoichiometric cyclometalation at Ni, but in all cases much longer reaction times and/or higher temperatures were required.

4.2.2 Protonation of the Ni-C bond

\[
\text{Scheme 4.3: Selective protonation of the Ni-C bond in 3}^{\text{CH}_2} \text{ and 3}^{\text{O}} \text{ to generate cationic derivatives 4}^{\text{CH}_2} \text{ and 4}^{\text{O}} \text{ with a coordinative Ni-(C-H) interaction.}
\]

Addition of an equimolar amount of ethereal HBF$_4$ to a yellow toluene solution of 3$^{\text{CH}_2}$ led to instantaneous precipitation of a purple-blue solid (Scheme 4.3). A similar reaction is observed when HBF$_4$ is added to 3$^{\text{O}}$ and a purple solid was isolated. ESI-MS suggests the formation of mononuclear cationic species with a reprotonated ligand fragment. When 4$^{\text{CH}_2}$ was redissolved in CH$_2$Cl$_2$, a band at $\lambda$ 577 nm ($\varepsilon = 4.2 \cdot 10^2$ L·mol$^{-1}$·cm$^{-1}$) was observed in the visible region of the UV-vis spectrum (for 4$^{\text{O}}$: $\lambda$ 535, $\varepsilon = 7.4 \cdot 10^2$ L·mol$^{-1}$·cm$^{-1}$). NMR spectroscopy ($^{31}$P, $^1$H or $^{13}$C) proved ineffective for both complexes, suggestive of solution-state paramagnetism. Single crystals were grown by layering pentane onto a concentrated CH$_2$Cl$_2$ solution and X-ray diffraction corroborated the solid-state structures of complexes 4$^{\text{CH}_2}$ and 4$^{\text{O}}$ to be formulated as [NiBr($\kappa^3$-P,N,(C-H)-1)]BF$_4$ (Figure 4.3). The molecular structures display a slightly distorted square planar Ni-center, which has a coordinative interaction with an aromatic C-H bond ortho to the pyridine ring. The proton involved in this interaction was located in the difference Fourier map. The Ni1-H1 contact distance of 2.12(4) Å (Ni1-C1 2.407(4) Å) for 4$^{\text{CH}_2}$ and 2.02(9) Å (Ni1-C1 2.355(8) Å) for 4$^{\text{O}}$ are shorter than the van der Waals radii (3.3 Å for Ni···C), indicating an interaction between Ni and the C-H bond. Furthermore, a $\pm 10^\circ$ tilting of H1 from the aromatic plane is observed for both complexes, which is a feature that is present in related complexes with an M-(C-H) interaction. The closest related structure for a Ni-complex is a cationic nickel benzoporphyrin, which shows a Ni-(CH) distance of $\sim$2.4 Å. For complexes 4$^{\text{CH}_2}$ and 4$^{\text{O}}$, the Ni-P1, Ni-N1 and Ni-Br1 bonds are slightly contracted relative to complexes 3.

Usually NMR is a very helpful tool for the characterization of agostic complexes. Commonly, the agostic proton and carbon experience an upfield shift in $^1$H NMR and $^{13}$C NMR and also the $^1$J$_{\text{CH}}$ becomes lower due to weakening of the C-H bond. However,
the crude mixture as well as the crystallized complexes $\text{4CH}_2$ and $\text{4O}$ always gave very broad and unresolved $^1\text{H}$ NMR spectra. On closer inspection of the crystallized material, it was noticed that two types of crystals were present, not only the purple/blue ones but also white crystals. Furthermore, on some occasions, the purple crystals decolored from the edges inwards even while they were submerged in mounting oil, which shows that the compound is inherently unstable. The white crystals turned out to be free ligand, protonated at the phosphorus, which means that in the total mixture there must also be 'naked' nickel particles present, that will make the solution of the mixture paramagnetic. To circumvent this problem, complex $\text{4CH}_2$ and $\text{4O}$ were synthesized via bromide abstraction from $\text{2CH}_2$ and $\text{2O}$ with AgBF$_4$ in CH$_2$Cl$_2$. Crystallization resulted in pure material for $\text{4CH}_2$, which still decomposed over a period of days in mounting oil. Remarkably, the crystals for $\text{4O}$ still could not be obtained in pure form and contained large amounts of white side-product.

The pure crystals of $\text{4CH}_2$ unfortunately still produced unresolved $^1\text{H}$ NMR spectra. The geometry in the solid state is square planar and should account for a diamagnetic complex, but the geometry in solution might be T-shaped or tetrahedral. By analysing the pure material, it could finally be concluded that $\text{4CH}_2$ is paramagnetic in solution and has a magnetic moment $\mu_{\text{eff}}$ in CD$_2$Cl$_2$ of 1.82 $\mu_B$, which is significantly smaller than the value for $\text{2CH}_2$ of 3.29 $\mu_B$. This could indicate that the geometry in solution is distorted square planar. It was anticipated that cooling of the solution might trap the Ni complexes in their square planar geometry, which would result in more defined NMR spectra, but no changes in the $^1\text{H}$ NMR spectrum are observed upon cooling to -90 °C. This is in agreement with the result obtained for the analogous Rh complex described in Chapter 2, in which the phenyl ring could also still freely rotate even at
-90 °C.

When NEt$_3$ is added to a suspension of pure complex 4$^{\text{CH}_2}$ in toluene, an immediate color change from blue to yellow is observed. NMR indicates that complex 3$^{\text{CH}_2}$ is regenerated albeit only ± 80% pure, based on $^{31}$P NMR spectroscopy. The fact that the ortho-C-H bond can now be deprotonated within seconds suggests that the Ni-(C$_{\text{Ph}}$H) interaction makes the C-H bond more acidic than the same bond in complex 2$^{\text{CH}_2}$ and facilitates cyclometalation. Complex 4$^{\text{O}}$ shows similar behaviour when NEt$_3$ is added to a toluene suspension, although this experiment had to be carried out without purification of 4$^{\text{O}}$ due to the instability of this complex.

4.2.3 DFT calculations

Intrigued by the observation of the rare Ni-(C$_{\text{Ph}}$-H) interaction in the solid state, we were motivated to understand the bonding in complex 3 and therefore studied this by means of DFT calculations. Because it was observed that the C-H bond in complexes 4 can be deprotonated much more easily compared to complexes 2, we wondered if this could be the result of a bonding interaction with the metal. As was discussed in Chapter 1, agostic interactions weaken the involved C-H bond by simultaneous electron-donation from the C-H $\sigma$-bond to the metal and $\pi$-back donation from the metal in the C-H $\pi^*$-orbital.

Recently it was reported by Alikhani et al. that a combination of quantum theory atoms in molecules (QTAIM) and electron localization function (ELF) topological analysis can be used to qualitatively and quantitatively describe the character of M-(C-H) interactions.$^{54}$ With QTAIM, a bond critical point (BCP) can be determined. Bonding between two atoms in indicated by a bond path at the interatomic surface of electron density at which the electron density is a maximum. Along this bond path, there is a BCP where the shared electron density reaches a minimum (a saddle point). The value of electron density at the BCP, $\rho_{\text{BCP}}$, is an approximate measure for the amount of electron density built up in the bonding region and as such may be taken as characteristic of the bond strength.

ELF topological analysis is a tool that measures electron localization in atomic and molecular systems in a way that corresponds to the VSEPR electronic domains and is therefore chemically intuitive. It is often used for describing bonding situations between donor-acceptor interactions, because it shows a clear separation between the core and valence electrons and shows covalent bonds and lone pairs. ELF topological analysis partitions the molecular space in so-called basins. The valence basins are characterized by the number of atomic valence shells to which they participate, which is called the synaptic order. A monosynaptic valence basin corresponds to a lone pair, whereas a disynaptic basin corresponds to a bond between two atoms. For agostic interactions a trisynaptic basin can be found, V(C,H,M), belonging to the valence shells of the three atoms. The population of this basin is a measure for the strength of the interaction. Moreover, the contribution of the metal core electrons to the basin is also an important measure to describe the strength of the interaction. High contributions of the metal core basins indicate a stronger interaction.

These kind of studies were recently performed to describe the interaction between Rh$^I$ and a protonated electron-poor PCP ligand.$^{55}$ Inspired by this report, we analyzed
the topology of electron density within the QTAIM and the topology of ELF for complexes 4 (Table 4.1). The results for complexes 4 are compared to a [Rh(I)(PCHP)(CO)]⁺ complex, for which an evident agostic interaction was reported.\(^{55}\)

The features of the solid state structures of 4(CH₃) and 4(O) are well-reproduced by DFT calculations in the singlet state. The computed Ni-Cl and Ni-H1 distances (2.402 Å and 2.155 Å for 4(CH₃) and 2.364 and 2.094 Å for 4(O)) are nearly identical to the metric parameters obtained from X-ray diffraction. The tilting of H1 from the planar phenyl ring (−10°) is very similar to that observed in the solid state structure. In both complexes, the Cl-H1 bond length is elongated with respect to that in the free ligand (from 1.085 to 1.097 Å for 4(CH₃) and to 1.099 Å for 4(O)), which indicates a weakening of the C-H bond. Furthermore, the Cl-H1 stretching frequency decreases relatively to the free ligand (from 3233 to 3094 cm\(^{-1}\) for 4(CH₃) and 3071 cm\(^{-1}\) for 4(O)), which is another indication of weakening of the C-H bond. These observations, along with the H1 tilting, are indicative of an interaction between nickel and the C-H bond.

\[\text{Figure 4.4: DFT calculated contour map of electron charge density, } \rho(r), \text{ of complex 4(O) showing the BCP at the blue dot.}\]

\[\text{Figure 4.4} \text{ shows the computed density map for a plane that contains Ni and the } C_{\text{Ph}}-H \text{ fragment of complex 4(O). One bond critical point (BCP) linking the Ni and Cl atoms was determined (indicated by a blue dot). According to QTAIM theory, a chemical bond exists if a line of locally maximum electron density links two neighboring atoms and also if along that line there is a BCP, evidencing in this case a Ni-(η\(^1\)-C1) interaction. Noteworthy is the curving of the bond path toward H1, which indicates that two charge density maxima, corresponding to the Ni···H1 and Ni···Cl BCPs, and a minimum, corresponding to the ring critical point (RCP), were very closely situated and have collapsed into one maximum. At the BCP, the low value of the electronic charge density, } \rho(r), \text{ and the low and positive values of the Laplacian of the charge density, } \nabla^2 \rho(r), \text{ are indicative of closed shell-type interaction (instead of a covalent interaction).}\]

With ELF analysis a disynaptic V(M,C) attractor was found between nickel and aromatic carbon Cl, indicating an electron-sharing interaction between those atoms.\(^{55\text{-}56}\) This topology is analogous to that reported for [Rh(I)(PCHP)]⁺, wherein a Rh-(η\(^1\)-C₇H₈) interaction with a concomitant agostic η\(^2\)-(C,H) interaction was proposed.\(^{55\text{-}56}\)
However, the population of the $V(M,C)$ basin in $4^O$ (0.16 e) is lower than in $[\text{Rh}^{I}(\text{PC}^\#\text{P})]^+$ (0.31 e), suggesting that the bonding situation in $4^O$ is closer to an anagostic $\eta^1$-C interaction.

Figure 4.5: ELF localization domains ($\text{ELF} = 0.81$) for $4^O$ and the disynaptic $V(\text{Ni,C}_{Ar})$ attractor with a populated basin of 0.16 e.

For complex $4^\text{CH}_2$ no valence attractor could be found with ELF analysis, suggesting that there is no significant electron sharing between the $C_{Ar}$-H and Ni. The other parameters that are compared in Table 4.1 are similar for complex $4^\text{CH}_2$ and $4^O$, although the values found for $4^\text{CH}_2$ are lower in all cases. These results suggest that the interaction in $4^O$ is somewhat stronger compared to that found in $4^\text{CH}_2$. This could be due to the more electron-withdrawing character of the phosphinite ligand which would produce a more electron-deficient metal center and enhance the stabilization through an agostic interaction.

The procedure to evaluate this type of intramolecular bond strengths is not straightforward. One way to estimate it is by calculating the energy difference of the structure displaying a Ni-(CH) interaction and a conformer lacking this binding motif; in this case, by determining the transition state for aryl rotation. The computed free energy barrier is very low at 4.2 kcal-mol$^{-1}$, indicative of a weak interaction. This is in agreement with the previous observation for the $[\text{Rh}^{III}(\text{PNC-H})(\text{CO})]BF_4$ complex reported in Chapter 2, showing fast rotation around $C_{Ph}$-$C_{Py}$ even at -90 $^\circ$C. Alikhani et al. recently proposed several criteria based on geometric, spectroscopic and QTAIM parameters to classify the strength of agostic bonding as anagostic, weak-to-medium agostic, medium-to-strong agostic or pre-hydride. Table 4.1 compares these geometric and spectroscopic parameters, and the results of QTAIM and ELF analysis for $4^\text{CH}_2$, $4^O$, and the reported Rh complex. Furthermore, three normalized parameters proposed by Alikhani et al. to classify the strength of agostic bonding are included. They consist of the ratio between the C-H$\text{agostic}$ distance and the H$\text{agostic}$···TM distance, the ratio between the stretching frequency of C-H$\text{agostic}$ bond in the complex and in the free ligand, and the ratio between the electron density at the BCP, $\rho_{\text{BCP}}$, for the C-H bond in the complex and in the free ligand.

The computed values for complex $4^\text{CH}_2$ and $4^O$ provide a mixed situation. The geometric parameters fulfill the criteria set for a weak-to-medium agostic C-H interaction, but the spectroscopic and topological parameters do not, showing values typical of
Table 4.1: Geometric, spectroscopic, energetic, QTAIM and ELF parameters for several [NiBr($\kappa$\textsubscript{3}-PN(CH)-L\textsuperscript{H})\textsuperscript{+}] complex and [Rh\textsuperscript{+}(PCHP)(CO)]\textsuperscript{+} pincer complex.

<table>
<thead>
<tr>
<th>parameter</th>
<th>complex 4\textsuperscript{CH\textsubscript{2}}</th>
<th>complex 4\textsuperscript{O}</th>
<th>[Rh\textsuperscript{+}(PCHP)(CO)]\textsuperscript{+}</th>
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<tr>
<td>Distances in Å, angles in °, and distance ratio</td>
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<td></td>
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<tr>
<td>d(C···M)</td>
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<td>d(C-H)</td>
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<td>1.099</td>
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<td>0.56</td>
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<td>Vibrational frequencies in cm\textsuperscript{-1}, and frequency ratio</td>
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<tr>
<td>ν(C-H)</td>
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<td>3071</td>
<td>2807</td>
</tr>
<tr>
<td>ν(C-H) / ν(C-H\textsubscript{free L})</td>
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<td>0.95</td>
<td>0.88</td>
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<td>Electron density, ρ, and Laplacian, \nabla\textsuperscript{2}ρ, at the bond critical points (BCP) in a.u.; and \nabla\textsuperscript{2}ρ\textsubscript{BCP} ratio</td>
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<tr>
<td>ρ\textsubscript{BCP}, \nabla\textsuperscript{2}ρ\textsubscript{BCP}(C···M)</td>
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<td>0.062, 0.215</td>
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<td>ρ\textsubscript{BCP}(C-H) / ρ\textsubscript{BCP}(C-H\textsubscript{free L})</td>
<td>0.96</td>
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<td>0.90</td>
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<td>ELF population of valence basins in a.u.</td>
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<tr>
<td>V(C,M)</td>
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anagostic bonding. We therefore tend to favor the description of a Ni-(C\textsubscript{Ph}-H) interaction in the solid state with predominant Ni-(\kappa\textsubscript{1}-C\textsubscript{Ph}) character for both complexes.

### 4.2.4 Attempts to produce more stable complexes with an Ni-(C\textsubscript{Ph}-H) interaction

One of the possible reasons that complexes 4\textsuperscript{CH\textsubscript{2}} and 4\textsuperscript{O} produce broad signals in NMR could be caused by paramagnetism in solution due to a (high spin) triplet state induced by the low-field bromide ligand. In general, π-donors such as bromides produce a small energy gap between the d-orbitals, which often results in high-spin complexes. It was studied if diamagnetic Ni-(C\textsubscript{Ph}-H) complexes could be obtained when π-acceptor co-ligands are used and if these complexes would also be more stable. Therefore, complexes 5 and 6 containing a -CN and -NO\textsubscript{2} group, respectively, were synthesized by simple salt metathesis with complex 2\textsuperscript{CH\textsubscript{2}} and AgCN or NaNO\textsubscript{2} (Scheme 4.4). To elucidate the coordination mode of the NO\textsubscript{2} ligand in complex 6, crystals were grown from CH\textsubscript{2}Cl\textsubscript{2}/pentane. The solid state structure confirmed coordination through the nitrogen instead of the more uncommon \kappa\textsubscript{1}-O or \kappa\textsubscript{2}-O binding mode. The \kappa\textsubscript{1}-N mode is also in agreement with the IR frequencies found for the nitrite ligand (1348 and 1373 cm\textsuperscript{-1}).
Addition of an equimolar amount of ethereal HBF$_4$ to a yellow toluene solution of complex 5 resulted in the precipitation of a red oily substance. This crude product showed again very broad signals in $^1$H NMR and no observable signal in $^{31}$P NMR in CD$_2$Cl$_2$. To exclude the possibility that the broadening is due to the presence of paramagnetic side product, it was attempted to purify the crude mixture by crystallization from CH$_2$Cl$_2$ and pentane. Unfortunately, despite several attempts, crystalline material was never obtained and proof for the Ni-(C$_{Ph}$-H) species were not obtained.

The same reaction was carried out with yellow complex 6 and again a brown precipitate was obtained. This time, however, crystallization from CH$_2$Cl$_2$/pentane resulted in the formation of red needles (amongst also brown precipitate), which give well-defined diamagnetic NMR spectra when dissolved in CD$_2$Cl$_2$. $^{31}$P NMR shows a signal at $\delta$ 64 ppm, which is in the expected region, but the aromatic region in $^1$H NMR integrated for seven protons whereas eight are expected. Furthermore, the complex seems to have lost $C_2$ symmetry, as two different signals are observed for both the CH$_2$(P) linker and the tert-butyl groups. These anomalies were explained when the corresponding crystal structure was resolved with X-ray diffraction and a totally different structure 7 was obtained than the expected agostic complex [Figure 4.7 and Scheme 4.5].

The formation of product 7 is interesting and not straightforward to understand; in particular the nitrite degradation and the formation of the two C-N bonds to the same bridging amide are peculiar. There is a formal loss of HNO$_3$, but it is unlikely that this
Figure 4.7: ORTEP (ellipsoids set at 50% probability) for complex 7. Selected bond lengths [Å] and angles [°] for 7: P2-Ni2 2.1894(6); N2B-Ni2 1.915(2); Ni2-Ni2 1.945(2); Ni2-O12 1.872(2); O12-Ni1 1.870(2); Ni1-Ni2 1.950(2); Ni1-N2A 1.917(2); P1-Ni1 2.1945(7); Ni1-Ni2 2.9063(6); Ni2-O12-Ni1 101.91(8); Ni1-Ni2-Ni2 96.51(8); N2B-Ni2-Ni2 93.55(8); N2B-Ni2-P2 86.03(6); N2A-Ni1-Ni2 93.30(8); P1-Ni1-N2A 86.31(6); P1-Ni1-O12 100.28(6); O12-Ni2-P2 99.57(6); C1A-N12-C1B 115.1(2).

Scheme 4.5: Unexpected formation of bimetallic product 7 from the reaction of complex 6 with ethereal HBF₄.

is expelled as a nitric acid molecule. It is plausible that the nitrite ligand is protonated by HBF₄ instead of the Ni-C bond. For Cu and Fe, acid-induced nitrite reduction from Mn-NO₂ to NO(g) and Mₙ⁺-OH species are well-known. Moreover, with two equiv. of acid, H₂O and Mₙ⁺⁺-NO species can be formed.57 Because complex 7 is not formed in quantitative yield (only 10% could be isolated pure), complex 6 might have reacted with two equiv. of HBF₄ and both mechanisms are still optional. In order to get more insight in the mechanism it was studied if this type of reactivity is limited to the use of HBF₄ as reagent and the reaction was also carried out with one equiv. of triflic acid. The triflate counter ion is more coordinating than BF₄ and could prevent formation of the bimetallic product, but according to NMR the same bimetallic Ni complex was obtained. Unfortunately, up to now, it remains unclear how this product is formed.
4.3 Conclusions

The P,N,C$_{Ph}$-ligand structure of 1$^{CH_2}$ and 1$^O$ facilitates base-induced C-H activation of the flanking phenyl-group at Ni$^{II}$ under mild conditions, although a specific solvent/base combination of toluene and NEt$_3$ was necessary to obtain the products 3$^{CH_2}$ and 3$^O$ in pure form. The isolation of these cyclometalated products allowed us to study their structural and spectroscopic properties. This is the first example of such facile C-H activation at Ni$^{II}$ that is not forced by the ligand structure, as is the case in e.g. ECE pincer complexes.

Additionaly, complexes 3$^{CH_2}$ and 3$^O$ are susceptible to reprotonation with HBF$_4$ generating the structurally characterized cationic complexes 4$^{CH_2}$ and 4$^O$ that have an Ni-(C$_{Ph}$-H) interaction in the solid state. The nature of this type of interaction is investigated by QTAIM and ELF calculations, which suggest the existence of a bona fide albeit weak (an)agostic coordinative interaction with predominant Ni-(η$^1$-C$_{Ph}$) character for complex 4$^{CH_2}$ and 4$^O$, although the interaction in 4$^O$ is somewhat stronger. Complexes 4$^{CH_2}$ and 4$^O$ react with NEt$_3$ within seconds to regenerate cyclometalated 3$^{CH_2}$ and 3$^O$ which is testament to increased acidity and reactivity of the C-H bond engaging in the Ni-(C$_{Ph}$-H) interaction compared to the analogous C-H bond complexes 2$^{CH_2}$ and 2$^O$.

By substituting the bromide ligand in 2$^{CH_2}$ for π-accepting ligands -CN and -NO$_2$, it was attempted to obtain cationic complexes that are more stable and diamagnetic in solution. However complexes 5 and 6 did not produce products with a Ni-(C$_{Ph}$-H) interaction when reacted with HBF$_4$. Possibly, the formation of these complexes is hampered by protonation at other positions in the complex than the Ni-C$_{Ph}$ bond.

The obtained insights on the C-H activation with simple Ni$^{II}$-precursors could possibly lead to the development of C-H functionalization methodologies involving a broader substrate scope.

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4.4 Experimental section

**General methods.** All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Reagents were purchased from commercial suppliers and used without further purification. THF, pentane, hexane and Et$_2$O were distilled from sodium benzophenone ketyl, CH$_2$Cl$_2$ was distilled from CaH$_2$, toluene from sodium under nitrogen. NMR spectra ($^1$H, $^{31}$P, and $^{13}$C($^1$H)) were measured on a Bruker DRX 500, Bruker AV 400, Bruker DRX 300 or on a Bruker AV 300 spectrometer. IR spectra (ATR mode) were recorded with a Bruker Alpha-p FT-IR spectrometer. High resolution mass
spectra were recorded on a JMS-TI00GCV mass spectrometer using field desorption (FD), or JEOL AccuTOF LC, JMS-TI00LP mass spectrometer using electron-spray ionization (ESI or CSI). Elemental analyses were carried out by Mikroanalytisches Laboratorium Kolbe.

**Synthesis of ligand 1-O.** To a solution of 6-phenyl-2-pyridone (0.64 g, 3.7 mmol), \(N,N,N',N'\)-tetramethylethylenediamine (1.1 mL, 7.4 mmol, 2 equiv.) and NEt\(_3\) (1.6 mL, 11.1 mmol, 3 equiv.) in THF (30 mL) was added di-tert-butylchlorophosphine (0.74 mL, 3.9 mmol) dropwise after which the mixture was refluxed for 1 week. The solvent was removed by syringe and the remaining solids were washed with pentane (10 mL). Toluene (15 mL) and NEt\(_3\) (2 equiv.) were added and the mixture was stirred at 50 °C for 1 h. After cooling, toluene was evaporated and the yellow product was extracted with THF (20 mL), filtered and evaporated to dryness to yield the product as a white oil (1.10 g, 94%).

**Synthesis Ni(Br)\(_2\)(x\(^2\)P,N-1-CH\(_2\)\(^3\) (2-CH\(_2\)).** Ligand 1\(^{CH2}\) (66 mg, 0.21 mmol) was dissolved in toluene (6 mL) and NiBr\(_2\)(DME) (56 mg, 0.18 mmol) was added. After stirring for 30 min., pentane was added (2 mL) to precipitate the product. The solvents were removed by syringe and the product was washed with pentane (3 mL) to yield 2\(^{CH2}\) as a purple product (0.54 g, 74%) and crystals suitable for X-ray analysis. HRMS (ESI): \(m/z\) calc. for C\(_{19}\)H\(_{26}\)NOP: 316.1830 [M+H]\(^+\); found: 316.1827.

**Synthesis Ni(Br)\(_2\)(x\(^2\)P,N-1-O\(^4\)) (2\(^{O}\)).** Ligand 1\(^{O}\) (0.45 g, 1.40 mmol) was dissolved in CH\(_2\)Cl\(_2\) (10 mL) and NiBr\(_2\)(dme) (0.42 g, 1.36 mmol) was added. After stirring for 30 min, the solvent was evaporated and the remaining solids were washed with pentane (10 mL). Slow evaporation of a CH\(_2\)Cl\(_2\)/pentane solution yielded the brown product (0.54 g, 74%) and crystals suitable for X-ray analysis. HRMS (ESI): \(m/z\) calc. for C\(_{19}\)H\(_{26}\)BrNNIOP: 454.0263 [M-Br]\(^+\); found: 454.0245. UV-Vis (CH\(_2\)Cl\(_2\), nm): \(\lambda\) 294 (\(\varepsilon = 1.3 \times 10^4\) L·mol\(^{-1}\)·cm\(^{-1}\)), \(\lambda\) 344 (\(\varepsilon = 3.6 \times 10^3\) L·mol\(^{-1}\)·cm\(^{-1}\)), \(\lambda\) 400 (\(\varepsilon = 1.6 \times 10^3\) L·mol\(^{-1}\)·cm\(^{-1}\)), \(\lambda\) 513 (\(\varepsilon = 1.9 \times 10^3\) L·mol\(^{-1}\)·cm\(^{-1}\)). Elemental analysis (%): calc for C\(_{19}\)H\(_{26}\)BrNNIOP: C 45.16, H 5.31, N 2.63; found: C 45.00, H 5.55, N 2.59. \(\mu_{eff}\) = 3.01 \(\mu\)B.

**Synthesis of Ni(Br)\(_2\)(x\(^3\)P,N,C-1-CH\(_2\)) (3\(^{CH2}\)).** Ligand 1\(^{CH2}\) (0.21 g, 0.67 mmol) was dissolved in toluene (10 mL) and NiBr\(_2\)(DME) (0.20 g, 0.64 mmol) was added. After stirring the purple suspension for 30 min, the solvent was removed by syringe and the remaining solids were washed with pentane (10 mL). Toluene (15 mL) and NEt\(_3\) (0.9 mL, 6.4 mmol, 10 equiv.) were added and the mixture was stirred at 50 °C for 1 h. After cooling, toluene was evaporated and the yellow product was extracted with THF (15 mL) and filtered. Evaporation of the solvent yielded complex 2\(^{CH2}\) (0.27 g, 93%). Crystals
suitable for X-ray diffraction were grown by layering with CH₂Cl₂/pentane. ¹H NMR (500 MHz, CD₂Cl₂, ppm): δ 7.97-7.91 (m, 1H, Ph-CH), 7.71 (t, J = 7.7 Hz, 1H, Py-CH), 7.41 (d, J = 7.9 Hz, 1H, Py-CH), 7.31 (dt, J = 7.5, 1.9 Hz, 1H, Ph-CH), 7.08 (m, 3H, Py-CH, 2Ph-CH), 3.24 (d, Jₚ = 8.0 Hz, 2H, CH₂P), 1.48 (d, Jₚ = 13.1 Hz, 18H, (CH₃)₂CP). ³¹P NMR (202 MHz, CD₂Cl₂, ppm): δ 45.53. ¹³C NMR (126 MHz, CD₂Cl₂, ppm): δ 166.76 (δ, Jₚ = 8.7 Hz, Py-C), 163.94 (d, Jₚ = 10.5 Hz, Py-C), 156.28 (d, Jₚ = 94.9 Hz, Ni-C), 147.66 (s, Ph-C), 138.80 (s, Ph-C), 138.31 (s, Ph-CH), 129.79 (d, Jₚ = 5.4 Hz, Ph-CH), 125.13 (s, Ph-CH), 122.10 (d, Jₚ = 3.9 Hz, Ph-CH), 120.23 (d, Jₚ = 8.3 Hz, Py-CH), 116.07 (s, Py-CH), 34.38 (d, Jₚ = 9.6 Hz, (CH₂)P), 33.28 (d, Jₚ = 14.4 Hz, (CH₃)CP), 29.32 (d, Jₚ = 4.1 Hz, (CH₃)CP). HRMS (FD): m/z calcd. for C₂₀H₂₇BrNiOP: 453.0398 [M⁺]; found: 451.0298.

Synthesis of Ni(Br)(κ³-P,N,C-1-O) (3⁰). Ligand ¹⁰ (0.57 g, 1.8 mmol) was dissolved in CH₂Cl₂ (6 mL) and NiBr₂(DME) (0.53 g, 1.7 mmol) was added. After stirring for 30 min., the solvent was evaporated and the remaining solids are washed with pentane (10 mL). Toluene (30 mL) and NEt₃ (2.4 mL, 17 mmol, 10 equiv.) were added and the mixture was stirred at 50 °C for 1h. After cooling, toluene was evaporated and the yellow product was extracted with Et₂O (60 mL) to yield analytically pure 2⁰ (0.59 g, 72%). Crystals suitable for X-ray diffraction were grown by layering with THF/pentane. ¹H NMR (300 MHz, MeCN-d₃, ppm): δ 7.90 (ddd, J = 8.4, 7.8, 0.8 Hz, 1H, Py-CH), 7.80 (m, 1H, Ph-CH), 7.44 (m, 1H, Ph-CH), 7.36 (dd, J = 7.7, 1.0 Hz, 1H, Py-CH), 7.20-7.08 (m, 2H, Ph-CH), 6.85 (dd, J = 8.0, 1.2 Hz, 1H, Py-CH), 1.56 (d, Jₚ = 14.2 Hz, 18H, (CH₃)₂CP), 1.48 (d, Jₚ = 4.1 Hz, (CH₃)CP). HRMS (FD): m/z calcd for C₁₉H₂₅BrNiOP: 453.01901 [M⁺]; found: 453.01918. UV-Vis (MeCN, nm): λ = 241 (ε = 2.2×10⁴ L·mol⁻¹·cm⁻¹), λ = 270 (ε = 3.3×10⁴ L·mol⁻¹·cm⁻¹), λ = 399 (ε = 9.1×10³ L·mol⁻¹·cm⁻¹). Elemental analysis (%): calcd for C₁₉H₂₅BrNiOP: C 50.38, H 5.56, N 3.09; found C 50.58, H 5.79, N 3.01.

Synthesis of [Ni(Br)(κ²-P,N-1-CH₂-H)]BF₄ (4⁶⁰). Complex ³⁶⁰ (20 mg, 0.044 mmol) was dissolved in toluene (2 mL) and 1 equiv. of HBF₄·Et₂O (6 μL, 0.044 mmol) was added slowly. The blue product precipitates directly and the remaining toluene was removed by syringe. The product was washed with pentane (1 mL) and was crystallized by layering with CD₂Cl₂/pentane. Despite several attempts the product could never be obtained as pure bulk material, due to the unstable nature of the product (even in crystalline form). However, some pure crystalline material could be separated and was used for X-ray analysis, mass analysis, UV-Vis spectroscopy and elemental analysis. HRMS (FD): m/z calcd for C₂₀H₂₇BrNiNP: 451.0398 [M⁺]; found 451.04085. UV-Vis (CH₂Cl₂, nm): λ = 240 (ε = 1.2×10⁴ L·mol⁻¹·cm⁻¹), 259 (ε = 1.2×10⁴ L·mol⁻¹·cm⁻¹), 338 (ε = 3.0×10³ L·mol⁻¹·cm⁻¹), 577 (ε = 4.2×10³ L·mol⁻¹·cm⁻¹). Elemental analysis (%): calcd for C₂₀H₂₇BrBF₄NiNP: C 44.58, H 5.24, N 2.60; found C 44.34, H 5.68, N 2.59. µₑₙ: 1.82 μB. Alternative synthesis: CH₂Cl₂ (2 mL) was added to complex ²⁶⁰ (20 mg, 0.038 mmol) and AgBF₄ (7.2 mg, 0.038 mmol) in a Schlenk. After 5 min., when the color had changed from purple to blue, the mixture was filtered. The volume was reduced to 0.5
CD 13.8 Hz, 18H, (CH$_3$)$_3$J mixture was filtered and the solvent evaporated to yield complex 6. The purple product precipitates directly and the remaining Et$_2$O was removed and the precipitation was washed with pentane (10 mL). Toluene (20 mL) was added and layered with pentane to crystallize the product (9 mg, 45%).

**Synthesis of [Ni(Br)(x²-P,N-1-O^h)]BF$_4$ (4O).** Complex 3O (30 mg, 0.066 mmol) was dissolved in Et$_2$O (5 mL) and 1 equiv. of HBF$_4$ · Et$_2$O (9 µL, 0.066 mmol) was added slowly. The purple product precipitates directly and the remaining Et$_2$O was removed by syringe. The product was washed with Et$_2$O (3 mL) and was crystallized by layering with CD$_2$Cl$_2$/pentane. Despite several attempts the product could never be obtained as pure bulk material, due to the unstable nature of the product (even in crystalline form). However, some pure crystalline material could be separated and was used for X-ray analysis, mass analysis, UV-Vis spectroscopy and elemental analysis. HRMS (ESI): m/z calcd for C$_{19}$H$_{26}$BrNiOP: 454.02684 [M+H]$^+$, found: 454.02973. UV-Vis (CH$_2$Cl$_2$, nm): λ 243 (ε = 2.2×10$^4$ L·mol$^{-1}$·cm$^{-1}$), λ 297 (ε = 1.3×10$^2$ L·mol$^{-1}$·cm$^{-1}$), λ 535 (ε = 7.4×10$^2$ L·mol$^{-1}$·cm$^{-1}$). Elemental analysis (%): calcd for C$_{19}$H$_{26}$BrNiOP: C 45.12, H 5.91, Br 35.27, N 2.59; found: C 45.15, H 5.08, N 2.34. Despite several attempts, this was the most accurate value found for complex 4O, due to the unstable nature of the crystals.

**Synthesis of Ni(CN)(x²-P,N,C-1-CH$_2$) (5).** Complex 3CH$_2$ (20 mg, 0.044 mmol) was dissolved in THF (2 mL) and AgCN (6 mg, 0.044 mmol) was added. The reaction was stirred for 30 min and filtered. Evaporation of the solvent yielded the product as yellow powder (25 mg, 71%). $^1$H NMR (300 MHz, acetone-d$_6$, ppm): δ 7.95-7.87 (m, 2H, Ph-CH and Py-CH), 7.69 (d, J = 7.9 Hz, 1H, Py-CH), 7.50 (dt, J = 7.4, 1.7 Hz, 1H, Ph-CH), 7.40 (d, J = 7.8 Hz, 1H, Py-CH), 7.13 (tt, J = 7.3, 1.6 Hz, 1H, Ph-CH), 7.06 (td, J = 7.4, 1.4 Hz, 1H, Ph-CH), 3.73 (d, $^3$J$_{CP}$ = 8.7 Hz, 2H, (CH$_3$)$_2$P), 1.49 (d, $^3$J$_{CP}$ = 13.6 Hz, 18H, (CH$_3$)$_3$CP). $^{31}$P NMR (300 MHz, acetone-d$_6$, ppm): δ 62.40. $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): δ 166.54 (d, $^3$J$_{CP}$ = 8.4 Hz, Py-C), 163.21 (d, $^3$J$_{CP}$ = 10.1 Hz, Py-C), 160.45 (d, $^3$J$_{CP}$ = 78.2 Hz, Ni-C), 148.39 (s, Ph-C), 140.34 (s, Ph-CH), 140.06 (s, Py-CH), 137.33 (d, $^3$J$_{CP}$ = 24.1 Hz, CN), 130.90 (d, $^3$J$_{CP}$ = 5.5 Hz, Ph-CH), 125.74 (s, Ph-CH), 122.78 (d, $^3$J$_{CP}$ = 3.4 Hz, Ph-CH), 120.50 (d, $^3$J$_{CP}$ = 9.1 Hz, Py-CH), 116.25 (s, Py-CH), 34.48 (d, $^1$J$_{CP}$ = 12.5 Hz, (CH$_3$)CP), 33.48 (d, $^1$J$_{CP}$ = 15.9 Hz, (CH$_2$)$_2$P), 29.25 (d, $^1$J$_{CP}$ = 4.4 Hz, (CH$_3$)CP). HRMS (ESI): m/z calcd. for C$_{21}$H$_{28}$N$_2$NiP: 397.1344 [M+H]$^+$; found: 397.1367.

**Synthesis of Ni(NO$_2$)(x²-P,N,C-1-CH$_2$) (6).** Ligand 1CH$_2$ (0.28 g, 0.89 mmol) and NiBr$_2$(dme) (0.23 g, 0.74 mmol) were dissolved in toluene (10 mL). The reaction was stirred for 30 min, during which a purple precipitate formed. The remaining toluene was removed and the precipitation was washed with pentane (10 mL). Toluene (20 mL) and NEt$_3$(1 mL, 7.5 mmol) were added and the reaction was stirred for 1 h at 50 °C, after which the solvent was evaporated. THF (20 mL) was added and the reaction mixture was filtered. Sodium nitrite (0.51 g, 7.5 mmol, 10 equiv.) was added and the reaction was stirred for 2 days. The solvent was evaporated and CH$_2$Cl$_2$(10 mL) was added. The mixture was filtered and the solvent evaporated to yield complex 6 as yellow solid (0.29 g, 94%). $^1$H NMR (300 MHz, acetone-d$_6$, ppm): δ 7.90 (t, J = 7.8 Hz, 1H, Py-CH), 7.65 (d, J = 7.8 Hz, 1H, Py-CH), 7.60-7.49 (m, 1H, Ph-CH), 7.29 (d, J = 7.7 Hz, 1H, Py-CH), 7.25-7.18 (m, 2H, Ph-CH), 6.84-6.76 (m, 1H, Ph-CH), 3.59 (d, $^2$J$_{PH}$ = 8.8 Hz, (CH$_2$)$_2$P), 1.53 (d, $^3$J$_{CP}$ = 13.8 Hz, 18H, (CH$_3$)$_3$CP). $^{31}$P NMR (121 MHz, acetone-d$_6$, ppm): δ 51.40. $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$, ppm): δ 167.84 (d, $^3$J$_{CP}$ = 8.3 Hz, Py-C), 164.78 (d, $^3$J$_{CP}$ = 9.1 Hz, Py-C), 162.47 (d, $^2$J$_{CP}$ = 74.1 Hz, Ni-C), 148.36 (s, Ph-C), 141.53 (s, Py-CH), 138.08 (s, Ph-CH), 132.49 (d, 90
Cyclometalation at Ni

5/CP = 5.0 Hz, Ph-CH), 127.46 (s, Ph-CH), 12.98 (d, 3/CP = 3.2 Hz, Ph-CH), 121.91 (d, 3/CP = 8.5 Hz, Py-CH), 11.97 (s, Py-CH), 36.44 (d, 1/JCP = 17.8 Hz, (CH2)P), 33.86 (d, 1/JCP = 17.8 Hz, (CH3)CP), 30.62 (d, 3/CP = 4.8 Hz, (CH3)CP). HRMS (ESI): m/z calcd. for C22H30N2NiP: 411.1500 [M-NO2+MeCN]+; found: 411.1522.

Synthesis of complex 7. To a solution of complex 6 (20 mg, 0.048 mmol) in toluene (7 mL) was added HBF4-Et2O (7 μL, 0.048 mmol). The product precipitated as brown solid and the supernatant was removed by syringe. The product was dried in vacuo and crystallized from CH2Cl2/pentane. The bright red single crystals were separated (14 mg, 10%) and were also suitable for X-ray analysis. 1H NMR (300 MHz, CD2Cl2, ppm): δ 7.93 (t, J = 7.9 Hz, 2H), 7.75-7.65 (m, 4H), 7.51 (td, J = 8.3, 1.4 Hz, 2H), 7.39-7.28 (m, 4H), 7.22 (d, J = 7.2 Hz, 2H), 4.46 (dd, J = 19.4, 6.3 Hz, 2H), 3.36 (dd, J = 19.4, 13.3 Hz, 2H), 1.64 (d, J = 14.6 Hz, 18H), 1.21 (d, J = 14.8 Hz, 18H). 31P NMR (121 MHz, CD2Cl2, ppm): δ 63.92. 13C NMR (126 MHz, CD2Cl2, ppm): δ 163.58 (d, 1/JCP = 4.9 Hz, Py-C), 157.63 (s, Ph-CN), 145.83 (t, 3/CP = 2.4 Hz, Py-C), 142.73 (s, Py-CH), 136.73-136.33 (m, Ph-C), 133.81 (s, Ph-CN), 133.17 (s, Ph-CH), 127.96 (s, Ph-CH), 127.13 (s, Ph-CH), 125.28-124.98 (m, Py-CH), 122.48 (s, Py-CH), 35.55 (d, 1/JCP = 12.9 Hz, (CH3)CP), 34.35 (d, 1/JCP = 19.6 Hz, (CH3)CP), 31.50 (d, 3/CP = 27.3 Hz, CH2P), 29.28 (s, (CH2)CP), 28.61 (s, (CH3)CP). HRMS (ESI, -30°C): m/z calcd. for C40H54N3Ni2OP2: 770.2449 [M-H+]++; found: 770.2471.

Determination of μeff by Evans’ method. For 2CH2, 5.9 mg of the complex was dissolved in 0.6 mL of acetone-d6 with a drop of CH2Cl2 and added to an NMR-tube. A capillary was filled with the same solution but without the paramagnetic complex and was inserted into the NMR-tube. The difference in shift of the CH2Cl2 signal was 119.91 Hz, measured at 400 MHz. For 2O, 6.6 mg of the complex was dissolved in 0.6 mL of CD2Cl2 with a drop of toluene. The difference in shift was 159.01 Hz, measured at 400 MHz. For complex 4CH2, 3.5 mg of the complex was dissolved in 0.6 mL of CD2Cl2 with a drop of toluene. The difference in shift was 19.44 Hz, measured at 300 MHz.

DFT calculations. Geometry optimizations and wave function generation for analysis were performed with Gaussian09 series of programs.58 We optimized [NiBr(κ3-PN1(C-H)-(tCH2))]2+ structure, and for comparison we computed a Rh1-P(CH)P pincer complex exhibiting a Rh-π1-C bonding with concomitant α-agostic γ1(C,H) bonding at the same level of Ni complex (see Table 4.1). The nature of the minima stationary points encountered was characterized by means of harmonic vibrational frequencies analysis. Full quantum mechanical calculations were performed within the framework of Density Functional Theory (DFT).59 by using the B3PW91 functional.60,61 The basis set for Ni, Rh, Br and P atoms was that associated with a pseudopotential,63 with a standard double-ξ LANL2DZ contraction, and the basis set was supplemented by f and d shells, respectively.64,65 The rest of atoms were described with a standard 6-31G(d,p) basis set.66,67 The MULTIWFN software69 was used for the topological analysis of electron density within the quantum theory atoms in molecules (QTAIM),70 and for the topological analysis of the electron localization function (ELF).71 In the theory of QTAIM, the value of the electron density (ρBCP) and the Laplacian of electron density (∇2ρBCP) are used to define the interactions presented in the molecules. For covalent interactions, the ρBCP and ∇2ρBCP are high and negative at the BCP, while for the closed-shell interactions
own a small value of $\varphi_{BCP}$ and a positive $\nabla^2\varphi_{BCP}$.

X-ray crystallography studies. X-ray intensities were measured on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator ($\lambda = 0.71073$ Å) and a CMOS Photon 50 detector at a temperature of 150(2) K. Intensity data were integrated with the Eval15 software. Absorption correction and scaling was performed with SADABS. The structures were solved with the programs SHELXT. Least-squares refinement was performed with SHELXL-2013 against $F^2$ of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.

For complex 6, all reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Cu Kα radiation ($\lambda = 1.54178$ Å) under the program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2014/7 and was refined on $F^2$ with SHELXL-2014/7. Analytical numeric absorption correction based on a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions (unless otherwise specified) using the instructions AFIX 23, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 $U_{eq}$ of the attached C atoms.

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were observed \[l=\sigma(l)\]. 224 Parameters were refined using 1 restraint. \(R_I/wR2\) \[l=\sigma(l)\]: 0.0222/ 0.0535. \(R_I/wR2\) [all refl.]: 0.0231/0.0540. \(S = 1.049\). Residual electron density found between -0.43 and 0.40 e/Å³.

3: \(C_{79}H_{25}BrNiOP\), Fw = 452.99, T = 150(2) K, dark-orange block, 0.30 × 0.20 × 0.15 mm³, monoclinic, \(P_{2_1}/n\) (no. 14), \(a = 10.3975(3), b = 31.1662(10), c = 12.4348(4), \beta = 103.2850°\). \(V = 3921.7(2) Å³\), \(Z = 8, D_{subx} = 1.534 \text{ g/cm}^3, \mu = 3.114 \text{ mm}^{-1}\). 32507 Reflections were measured up to a resolution of \((\sin \theta/\lambda)_{\text{max}} = 0.59 \text{ Å}^{-1}\). 6906 Reflections were unique (\(R_{\text{int}} = 0.0840\)), of which 4806 were observed \[l=\sigma(l)\]. 445 Parameters were refined using 444 restraints. \(R_I/wR2\) \[l=\sigma(l)\]: 0.0421/0.0706. \(R_I/wR2\) [all refl.]: 0.0820/0.0808. \(S = 0.990\). Residual electron density found between -0.42 and 0.53 e/Å³. CCDC: 1455564.

4: \(C_{20}H_{28}BrF_{4}NNiP\), Fw = 538.83, T = 150 K, blue plate, 0.60 × 0.20 × 0.10 mm³, monoclinic, \(P_{2_1}/n\) (no. 14), \(a = 14.243(3), b = 8.0781(17), c = 19.554(4) Å, \beta = 97.659(11)°\). \(V = 2229.8(8) Å³\), \(Z = 4, D_{x} = 1.605 \text{ g/cm}^3, \mu = 2.773 \text{ mm}^{-1}\). 12349 Reflections were measured up to a resolution of \((\sin \theta/\lambda)_{\text{max}} = 0.83 \text{ Å}^{-1}\). 4589 Reflections were unique (\(R_{\text{int}} = 0.0795\)), of which 3031 were observed \(l=\sigma(l)\). 312 Parameters were refined using 161 restraints (RIGU). \(R_I/wR2\) \[l=\sigma(l)\]: 0.0486/ 0.0860. \(R_I/wR2\) [all refl.]: 0.0957/0.0992. \(S = 1.024\). Residual electron density found between -0.54 and 0.79 e/Å³.

6: \(C_{20}H_{37}NiO_{2}P\), Fw = 417.11, T = 110 K, orange block, 0.22 × 0.18 × 0.15 mm³, monoclinic, \(P_{2_1}/c\) (no. 14), \(a = 7.33512(8), b = 14.13610(16), c = 18.60563(19) Å, \beta = 97.8321(10)°\). \(V = 1911.22(4) Å³\), \(Z = 4, D_{x} = 1.450 \text{ g/cm}^3, \mu = 2.39 \text{ mm}^{-1}\). 11461 Reflections were measured up to a resolution of \((\sin \theta/\lambda)_{\text{max}} = 0.616 \text{ Å}^{-1}\). 3737 Reflections were unique (\(R_{\text{int}} = 0.019\)), of which 3482 were observed \(l=\sigma(l)\). 241 Parameters were refined with no restraints. \(R_I/wR2\) \[l=\sigma(l)\]: 0.025/0.065. \(R_I/wR2\) [all refl.]: 0.027/0.066. \(S = 1.06\). Residual electron density found between -0.29 and 0.29 e/Å³.

7: \(C_{40}H_{58}N_{2}OP_{2}B_{2}F_{8}\), 1.843(CH₂Cl₂), Fw = 1103.38, T = 110 K, orange rod, 0.23 × 0.12 × 0.06 mm³, monoclinic, \(P_{2_1}/c\) (no. 14), \(a = 12.9959(2), b = 17.1122(3), c = 24.8497(4) Å, \beta = 94.1812(14)°\). \(V = 5511.58(16) Å³\), \(Z = 4, D_{x} = 1.330 \text{ g/cm}^3, \mu = 3.555 \text{ mm}^{-1}\). 34646 Reflections were measured up to a resolution of \((\sin \theta/\lambda)_{\text{max}} = 0.995 \text{ Å}^{-1}\). 10759 Reflections were unique (\(R_{\text{int}} = 0.031\)), of which 9327 were observed \(l=\sigma(l)\). 667 Parameters were refined with 299 restraints. \(R_I/wR2\) \[l=\sigma(l)\]: 0.043/0.109. \(R_I/wR2\) [all refl.]: 0.050/0.114. \(S = 1.03\). Residual electron density found between -0.65 and 1.11 e/Å³.
Figure 4.8: The difference Fourier contour map of complex 4°, which shows the location of H1, the proton that contributes to the C1-H1-Ni1 interaction.

References

Cyclometalation at NiII


[73] Sheldrick, G. SADABS; University of Göttingen, Germany 2008.