Fundamental reactivity of the Metal-Carbon bond in cyclometalated PNC-complexes
Jongbloed, L.S.

Citation for published version (APA):
5 Oxidation-induced $\text{C}_{\text{sp}}^{2}-\text{C}_{\text{sp}}^{3}$ Bond Formation from Cyclometalated Ni$^{\text{II}}$ Complexes

5.1 Introduction

Transition-metal-catalyzed cross-coupling has become one of the most used carbon-carbon and carbon-heteroatom bond-forming reactions in chemical synthesis. In the past decade, nickel has emerged as a valuable metal to catalyze a wide variety of C-C bond-forming reactions, such as Negishi, Suzuki-Miyaura, Stille, Kumada and Hiyama couplings. Next to 2$e^-$ processes, that are common for second and third row transition metals, nickel can also undergo 1$e^-$ processes, ensuring a wide range of accessible oxidation states during catalysis. The occurrence of Ni$^{\text{I}}$ and Ni$^{\text{III}}$, besides Ni$^{\text{0}}$ and Ni$^{\text{II}}$, allows for novel modes of reactivity and radical mechanisms. This different mode of reactivity has for example resulted in the use of secondary and tertiary alkyl halides as substrates in cross coupling reactions. This type of reactivity is considered difficult for classical Pd-catalysts. One downside of the presence of these paramagnetic Ni$^{\text{I}}$ and Ni$^{\text{III}}$ species is the decreased level of information to be gathered from NMR studies as a tool for mechanistic understanding. However, recently much progress has been made in this field, e.g. by theoretical investigations, the spectroscopic detection of intermediates by EPR or the use of well-defined model systems.

The results of these mechanistic studies show that one of the common pathways for the C-C product-forming step is reductive elimination from nickel in oxidation state Ni$^{\text{III}}$. Although the Ni$^{\text{III}}$ intermediates were never spectroscopically detected during catalysis, the isolation or spectroscopic detection of stabilized Ni$^{\text{III}}$ model systems that are relevant for C-C or C-X coupling reactions provided insight in the structure and reactivity of these intermediates. The stabilization of these Ni$^{\text{III}}$ complexes is induced by the use of specific ligand structures or the use of -CF$_3$ groups as model for alkyl substituents (see Scheme 5.1). The two approaches combined even allowed the isolation of stable Ni$^{\text{IV}}$ complexes that undergo reductive C-X bond formation by reaction with exogenous nucleophiles, thus establishing that Ni$^{\text{IV}}$ could also be a relevant oxidation state for cross-coupling reactions. More recently, it was reported that a challenging aryl-CF$_3$ coupling from Ni$^{\text{IV}}$ is possible using this approach.

As discussed in Chapter 2, the aromatic trifluoromethylation is industrially inter-
Scheme 5.1: Reported model systems that show controlled C-C bond formation from a high-valent Ni\textsuperscript{III} complex\textsuperscript{7} (A) or Ni\textsuperscript{IV} complex\textsuperscript{8} (B).

esting because of the intriguing properties of fluoroorganic materials, but synthetically cumbersome.\textsuperscript{13} For late TMs, the CF\textsubscript{3} substituent is usually very stabilizing and is therefore often not susceptible to reductive elimination.\textsuperscript{14} However, it was proposed that Ni could be an active catalyst for this transformation,\textsuperscript{15,16} and therefore, the precise understanding of Ni-CF\textsubscript{3} bonding and reactivity of these complexes have been subject to several studies, usually in comparison to Ni-CH\textsubscript{3} bonding.\textsuperscript{11-12,22} The main findings show that the lone pair of the CF\textsubscript{3} substituent has increased C 2s character and a stronger donation to the metal. Furthermore, the CF\textsubscript{3}-group usually stabilizes the metal-based HOMO and LUMO orbitals, which results in higher oxidation potentials compared to the corresponding CH\textsubscript{3}-complexes.

Scheme 5.2: (A) A recently reported C-H functionalization reaction catalyzed by Ni\textsuperscript{II} salts.\textsuperscript{23} The cyclometalated complex in brackets is a likely intermediate in the catalytic cycle, but it is unknown whether the C-C coupled product is formed from a Ni\textsuperscript{III} or Ni\textsuperscript{IV} intermediate. (B) our approach to investigate the relevance of Ni\textsuperscript{III} intermediates for C-C coupling from cyclometalated complexes.

Most previously reported mechanistic investigations and model systems for C-C coupling at Ni focus on cross-coupling reactions, in which the Ph-substituent can freely rotate around the M-Ph bond.\textsuperscript{24} In this Chapter, we report a study on the oxidatively induced C\textsubscript{sp\textsuperscript{2}}-C\textsubscript{sp\textsuperscript{3}} bond formation from cyclometalated Ni\textsuperscript{III} complexes, in which the rotation of the phenyl-group is constrained by the linkage to the adjacent pyridine.
moiety (see Scheme 5.2). These complexes represent model systems for the recently reported Ni-catalyzed C-H functionalization reactions of substrates with a bidentate 8-aminoquinoline directing group. 23,25 Besides one theoretical investigation of the mechanism of this type of reaction, 26 little information is available on the elementary steps for substrate activation and product formation. It is postulated that C-H functionalization is achieved via an NiII-NiIV cycle, but the involvement of NiIII intermediates could not be ruled out.

The cyclometalated complexes that are used for our study on C-C bond formation from Ni rely on the PONCPh ligand introduced in Chapter 4. Square planar (PNOC)NiII-R complexes that contain either a methyl- or trifluoromethyl-group are developed and subjected to oxidation with common 1e- oxidants. It was envisioned that the Ni-CF3 complex would be more stable than the Ni-CH3 complex and allow for the isolation of a NiIII intermediate. However, with the help of CV, EPR and spectroelectrochemistry, it was proven that both complexes undergo fast reductive elimination from the high-valent oxidation state at RT. Additionally, reduction of the (PNOC)NiII-R complexes to yield stable anionic complexes with ligand-centered radicals is discussed.

5.2 Results and Discussion

5.2.1 Synthesis of (CNOP)NiR complexes

Complexes 2CH3 and 2CF3 are both synthesized from complex 1, that was introduced in Chapter 3. The Me-group in complex 2CH3 can be easily installed via simple salt metathesis from MeLi and 1 (Scheme 5.3). Upon addition of MeLi to a solution of 1 in toluene, an immediate color change from yellow to red is observed. The product shows a small downfield shift in 31P NMR compared to complex 1 (δ 194 ppm vs 187 ppm) and in 1H NMR a new signal arises in the upfield region at δ -0.06 ppm (JPH = 9.1 Hz) which is assigned to Ni-CH3. Crystals suitable for X-ray analysis were grown by slow evaporation of an Et2O solution and the molecular structure shows Ni-CH3 bond lengths of 1.933(4) Å, 1.943(4) Å, 1.957(4) Å and 1.958(4) Å for the four independent molecules found in the asymmetric unit cell.

![Scheme 5.3](image)

Scheme 5.3: Synthesis of Ni-alkyl complexes 2CH3 and 2CF3 from complex 1.

Complex 2CF3 is prepared by reacting 1 with CsF and TMS-CF3, Ruppert’s reagent, in THF. Complex 2CF3 gives a quartet in 31P NMR at δ 195 ppm with a coupling constant of 9.1 Hz. Although the reactivity with 2e- oxidants is very interesting, as NiIV was recently proposed as a possible intermediate in C-C bond-forming processes, 8,12 some preliminary reactivity studies with e.g. Phl(OAc)2, PhlCl2, and S-(trifluoromethyl)dibenzothiophenium salts, indicated that these results were difficult to interpret. Therefore, this study lies outside the scope of this Chapter.
$^{3}J_{PF}$ of 26 Hz and a doublet at $\delta$ 11 ppm with the same coupling constant is found in $^{19}$F NMR. In $^{13}$C NMR, a signal is evident for the Ni-CF$_3$ at $\delta$ 144 ppm with a coupling constant $^{2}J_{CP}$ of 18 Hz and a large coupling constant $^{1}J_{CF}$ of 357 Hz, which is similar to other reported Ni-CF$_3$ complexes. In this case too, single crystals were grown by slow evaporation from an Et$_2$O solution and the molecular structure is very similar to complex $^{2}$CH$_3$ although the Ni-CF$_3$ bond is slightly contracted compared to Ni-CH$_3$ (1.878(3), $\Delta d$ vs NiCH$_3$ is at least 0.055 Å). This phenomenon is common and can be explained by the stronger binding of the CF$_3$-group to Ni.

Figure 5.1: ORTEP (ellipsoids set at 50 % probability) for complex $^{2}$CH$_3$ (left) and $^{2}$CF$_3$ (right). Four independent molecules in the asymmetric unit cell were found for $^{2}$CH$_3$ and one of them is depicted and described here. The other three can be found in the experimental section. Selected bond lengths [Å] and angles [°] for $^{2}$CH$_3$: For Ni1: Ni1 C12A 1.933(4); Ni1 C1A 1.925(3); Ni1 N1A 1.902(3); Ni1 P1A 2.151(1); C1A Ni1 N1A 84.0(1); C1A Ni1 C12A 93.4(2); C12A Ni1 P1A 99.7(1); P1A Ni1 N1A 83.0(1); C1A Ni1 P1A 166.7(1).

Another difference that is commonly found in literature when Ni-CH$_3$ complexes are compared to Ni-CF$_3$ complexes, is the stabilization of the HOMO and the LUMO by the CF$_3$ substituent. Whether this is also true for complexes $^{2}$CH$_3$ and $^{2}$CF$_3$ was investigated by DFT calculations. After structure optimization, the energy levels of the frontier molecular orbitals are determined. Table 5.1 shows the comparison of the energy levels of the HOMO and LUMO of $^{2}$CH$_3$ and $^{2}$CF$_3$. The calculated HOMO of complex $^{2}$CF$_3$ is stabilized by 0.5 eV relative to $^{2}$CH$_3$, which will probably result in a higher oxidation potential for $^{2}$CF$_3$. On the other hand, also the LUMO of $^{2}$CF$_3$ is stabilized by 0.3 eV, resulting in easier reduction.

The stabilizing effect of the CF$_3$-group was also demonstrated by mass spectrometry. While for complex $^{2}$CF$_3$ a molecular ion peak could be found with Electrospray Ionization (ESI) at $m/z$ 442.1077, only fragmented ion peaks were found for complex $^{2}$CH$_3$. With Field Desorption (FD), a method for which a softer ionization method is used and generally little or no fragmentation is observed, the same molecular ion peak was found for complex $^{2}$CF$_3$. For $^{2}$CH$_3$, still similar fragmentation was found with a main peak of $m/z$ 345.2762. This value could correspond to a methylated ligand structure that is oxidized at the phosphorus, as this fragment has a calculated mass of 345.1858. This result indicates that complex $^{2}$CH$_3$, in contrast to complex $^{2}$CF$_3$, is relatively un-
stable and undergoes reductive elimination (RE) upon ionization.

### 5.2.2 Electrochemistry

Because we want to study the behaviour of complexes $2^{\text{CH}_3}$ and $2^{\text{CF}_3}$ in the high-valent Ni$^{\text{III}}$ state, the oxidation potentials were determined with cyclic voltammetry, see Figure 5.2. For complex $2^{\text{CH}_3}$, the CV in PrCN shows an irreversible oxidation wave with a peak potential $E_{\text{ox}}$ of -0.08 V, which means that $2^{\text{CH}_3}$ can be oxidized by weak oxidants such as ferrocenium salts. The complete irreversibility of the wave suggests a follow-up chemical reaction of the oxidized Ni-complex. If the chemical reaction is slow, faster scan rates can sometimes result in more reversible waves, but this was not observed. Moreover, recording the voltammogram at low temperatures (-55 °C) did not help in stabilizing and observing the intermediate. Scanning to higher potentials revealed a second oxidation wave with a peak potential of $E_{\text{ox}}$ 0.77 V.

It was presumed that complex $2^{\text{CF}_3}$ would show different electrochemical behaviour as RE with Ph-CF$_3$ is more difficult. Ideally, $2^{\text{CF}_3}$ would show a reversible Ni$^{\text{II}}$/Ni$^{\text{III}}$ oxidation wave, which would imply that the electrochemical process is different from that of complex $2^{\text{CH}_3}$. However, an irreversible oxidation wave very similar to $2^{\text{CH}_3}$ is observed for $2^{\text{CF}_3}$ at $E_{\text{ox}}$ 0.51 V that, as expected, occurs at higher potentials compared to $2^{\text{CH}_3}$ ($\Delta E_{\text{ox}} = 0.59$ V). The fact that also this oxidation wave is completely irreversible suggests that similar electrochemical processes occur. This wave does not become more reversible at faster scan speeds or lower temperatures either. Furthermore, a second oxidation wave is observed at $E_{\text{ox}}$ 0.88 V, which is at similar potential as observed

### Table 5.1: DFT$^a$ calculated energy levels of the frontier orbitals of complexes $2^{\text{CH}_3}$ and $2^{\text{CF}_3}$.

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<th>LUMO (eV)</th>
<th>Gap (eV)</th>
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$^a$ Structures optimized with Turbomole (BP86, def2-TZVP, disp3).
for the second oxidation wave of complex $2^{CH_3}$ ($E_{ox} 0.77 \text{ V}$). This suggests that the intermediate formed after the first wave is similar in nature as the one for complex $2^{CH_3}$.

![Scheme 5.4: Intermediates that are possibly formed during the first oxidation wave in CV of complexes $2^{CH_3}$ and $2^{CF_3}$.](image)

The irreversibility of the first oxidation peaks of $2^{CH_3}$ and $2^{CF_3}$ could be caused by simple coordination of PrCN to the Ni$_{III}$ intermediate, as Ni$_{III}$ complexes do generally not adopt a square planar geometry. It could also be in agreement with fast Ph-R reductive elimination after 1e$^-$ oxidation to Ni$_{III}$ (A) to generate a Ni$_I$ species B [Scheme 5.4]. As this chemical reaction happens while scanning at a potential of at least -0.08 V, it is very likely that the putative Ni$_I$ species B is then directly oxidized to Ni$_{II}$ C. Such a electrochemical-chemical-electrochemical process is called an ECE mechanism. If this happens, two electrons are involved within the first oxidatin wave. A third possibility is fast homolytic cleavage of the Ni$_{III}$-R (R = CH$_3$ or CF$_3$) bond resulting in a R$^•$ radical and [(CNOP)Ni$_{II}$(PrCN)]$^+$. In order to rule out the possibility that homolytic Ni-R bond cleavage occurs after oxidation, complex 3 was synthesized by bromide abstraction from complex 1 with AgBF$_4$ and was subjected to a CV study as a verification that the second oxidation waves for $2^{CH_3}$ and $2^{CF_3}$ do not originate from complex 3. An oxidation wave at $E_{ox}$ 0.78 V is found that shows quasi-reversible behaviour with a lower and broadened reduction wave ($i_{pc}/i_{pa} = 0.27$). One of the logical explanations for this behaviour is the coordination of a solvent molecule (PrCN) to the Ni$_{III}$ intermediate. The oxidation wave of 3 occurs at the same potential as the second oxidation wave of $2^{CH_3}$, but occurs at a potential that is 0.11 V less positive than the second oxidation wave of $2^{CF_3}$. If homolytic bond cleavage had occurred, the exact same product (3) should have formed and the second oxidation wave should occur at the exact same potential. However, it is difficult to completely rule out homolytic Ni$_{III}$-R cleavage based on these results.

One marked difference between the voltammograms of $2^{CH_3}$ and $2^{CF_3}$ is the peak current, which is almost twice as high for $2^{CH_3}$ compared to $2^{CF_3}$. Such differences can be caused by a different number of electrons involved in the wave, i.d. 1e$^-$ or 2e$^-$ waves. However, the peak currents of a 1e$^-$ reversible reduction wave present in the voltam- mograms of both complexes (see section 2.6 and experimental section) show roughly
the same difference in peak current, implying that the difference in peak currents for complexes $2^{CH_3}$ and $2^{CF_3}$ does not stem from a difference in amount of electrons in a wave. Moreover, the peak current is dependent on the diffusion coefficients of the analyte, and the difference could be caused by a difference in the diffusion coefficients of the two complexes. However, it was shown by diffusion ordered NMR spectroscopy (DOSY) that complex $2^{CH_3}$ and $2^{CF_3}$ have very similar diffusion coefficients. Different approaches were used to understand the difference in peak current, such as bulk electrolysis and simulation of the cyclic voltammograms, but no conclusive answers were obtained to date.

5.2.3 UV/Vis spectroelectrochemistry

In order to get more insight in the electrochemical processes of complexes $2^{CH_3}$ and $2^{CF_3}$, UV/Vis spectroelectrochemistry (SEC) was carried out using an optically transparent thin layer electrolysis (OTTLE) cell. It was anticipated that this method could allow for the observation of possible intermediates that are formed after the first oxidation wave. As SEC is generally carried out with much lower scan rate (0.003 V s$^{-1}$) compared to CV, it was assumed that putative Ni$^{II}$ complex B would not be stable at the applied potential and would directly be oxidized to Ni$^{III}$ (C).

![Figure 5.3: UV-Vis spectroelectrochemical oxidation in MeCN/nBu$_4$NPF$_6$ solutions for complex $2^{CH_3}$ (a) and complex $2^{CF_3}$ (b); anodic scan from 0 V to +1.2 V and 0 V to +1.8 V (referenced to Ag/Ag$^+$), respectively.](image)

The UV/Vis spectrum of complex $2^{CH_3}$ exhibits a band in the visible region at 452 nm ($\varepsilon = 1.3 \times 10^3$ L·mol$^{-1}$·cm$^{-1}$) and two intense bands in the near-UV region at 313 nm ($\varepsilon = 7.8 \times 10^3$ L·mol$^{-1}$·cm$^{-1}$) and 241 nm ($\varepsilon = 1.7 \times 10^4$ L·mol$^{-1}$·cm$^{-1}$). According to TD-DFT calculated absorptions, most of these transitions are MLCTs, with one intraligand $\pi$-$\pi^*$ transition. Upon spectroelectrochemical oxidation of complex $2^{CH_3}$ in MeCN almost all bands disappear and only one marked band at 277 nm characterizes the oxidized product. The presence of two clear isosbestic points indicates a defined transition from the starting material to one oxidized product. However, in line with the
CV experiments, the oxidation process is irreversible and the starting spectrum was not regenerated upon reverse sweep.

![Figure 5.4](image)

**Figure 5.4:** (a) Experimental UV/Vis spectrum of complex 3. (b) TD-DFT calculated absorption spectrum of complex 2CH₃. (c) TD-DFT calculated absorption spectrum the expected Ni^{III} intermediate A. (d) TD-DFT calculated absorption spectrum the tetrahedral Ni^{II} product after RE C.  Structures are optimized with Turbomole, BP86, def2-TZVP, disp3, and absorption spectra are calculated with ORCA.

Complex 2CF₃ exhibits only bands in the near-UV region with a very intense band at 245 nm ($\varepsilon = 2.6 \cdot 10^4$ L·mol⁻¹·cm⁻¹) and some less intense bands at longer wavelengths (304 nm, $\varepsilon = 5.8 \cdot 10^3$ L·mol⁻¹·cm⁻¹, 340 nm, $\varepsilon = 5.3 \cdot 10^3$ L·mol⁻¹·cm⁻¹ and 395 nm, $\varepsilon = 1.3 \cdot 10^3$ L·mol⁻¹·cm⁻¹). The larger HOMO-LUMO gap calculated by DFT [Table 5.1] for complex 2CF₃ compared to 2CH₃ is in line with the observed hypsochromic shift of the longest wavelength band. Similar as for complex 2CH₃, most of the distinct bands disappeared on spectroelectrochemical oxidation of 2CF₃ leaving only one band at 271 nm. The resemblance of the spectra of both oxidized products indicates again that the same (or a closely related) product is formed in both processes.

By comparing the UV/Vis spectra obtained after oxidation of 2CH₃ and 2CF₃ to complex 3 (see [Figure 5.4a]), it becomes clear that 3 is not the product that is formed because the spectra do not overlap. Although complex 3 also exhibits a band around 271 nm ($\varepsilon = 3.5 \cdot 10^4$ L·mol⁻¹·cm⁻¹), the extinction coefficients differ roughly one order of magnitude. Furthermore, 3 exhibits a band at 342 nm that is not present in the spectra of the oxidized products.
In an attempt to identify the oxidized species, the UV/Vis spectra of the putative Ni$^{\text{III}}$ intermediate (A) and product (C) of the oxidation of 2$^{\text{CH}_3}$ are simulated by TD-DFT calculations and are depicted in Figure 5.4c,d. Both calculated spectra have absorptions in the visible region that are not present in the spectra obtained after oxidation of 2$^{\text{CH}_3}$ and 2$^{\text{CF}_3}$, suggesting that both species are not formed after oxidation. However, TD-DFT calculations do not always reproduce the actual spectra well and deviations in wavelengths and intensities can be found. As the predicted spectrum of 2$^{\text{CH}_3}$ also does not show great resemblance to the observed spectrum (Figure 5.4b), TD-DFT might not be a suitable method in this case for identification of the product.

5.2.4 Chemical oxidation

Because (spectro)electrochemistry provided some insights in the processes upon oxidation but no conclusive answers, we decided to investigate the chemical oxidation of complexes 2$^{\text{CH}_3}$ and 2$^{\text{CF}_3}$. As the electron transfer can be controlled by the addition of one equivalent of oxidant, further oxidation to species C (see Scheme 5.4) can be prevented and the oxidation should result in either Ni$^{\text{III}}$ species A or Ni$^{\text{I}}$ species B. These d$^{9}$ and d$^{7}$ species, respectively, both have one unpaired electron and can be observed by EPR spectroscopy.$^{\text{ii}}$

Scheme 5.5: The products that could be formed when 2$^{\text{CH}_3}$ and 2$^{\text{CF}_3}$ are oxidized with chemical oxidants. The reactions are carried out in the glovebox at RT in PrCN/MeCN (3:1) and are frozen in liquid N$_2$ as fast as possible. The oxidant used for complex 2$^{\text{CH}_3}$ is [Fe($\eta^5$-C$_5$H$_4$COMe)Cp]BF$_4$; for 2$^{\text{CF}_3}$ [thianthrenium]BF$_4$ is used.

The chemical oxidation of complex 2$^{\text{CH}_3}$ is carried out at RT in a mixture of PrCN/MeCN (3:1) with the mild oxidant [acetylferrocenium]BF$_4$ ([Fe($\eta^5$-C$_5$H$_4$COMe)Fc]BF$_4$). Although in principle ferrocenium$^+$ would be a strong enough oxidant, the slightly stronger acetyl-analogue should make sure that the oxidation is fast and quantitative. Upon addition to complex 2$^{\text{CH}_3}$, the dark blue color of the oxidant immediately disappears suggesting fast consumption. The resulting orange solution is transferred to an EPR tube and frozen in liquid N$_2$ as fast as possible.

The EPR spectrum (Figure 5.5a) is measured at 30 K and reveals a rhombic g-tensor with well-resolved hyperfine interactions with a single phosphorus atom (rhombic A-tensor). A satisfactory simulation of the experimental spectrum was obtained with the g- and A-tensor components shown in Table 5.2. The DFT computed EPR parameters of Ni$^{\text{I}}$ complex 5$^{\text{CH}_3}$ (geometry shown in Figure 5.5c) are in agreement with the experimental values. In particular the large phosphorus hyperfine couplings are well-

	$^{\text{ii}}$tetrahedral Ni$^{\text{III}}$ complexes in the triplet state have two unpaired electrons and are usually not observable with X-band EPR
Figure 5.5: (a) Experimental and simulated X-band EPR spectra of $\text{C}_3\text{H}_5$. The simulated spectrum was obtained using the parameters listed in Table 5.2. The experimental spectrum is recorded at 30 K in frozen PrCN/MeCN 3:1. Microwave frequency = 9.363973 GHz, modulation amplitude = 4 Gauss, microwave power = 2 mW. (b) Optimized geometry (Turbomole BP86, def2-TZVP, disp3) of Ni$^{\text{III}}$ precursor $\text{C}_3\text{H}_5$. (c) Optimized geometry of Ni$^{\text{II}}$ complex $\text{C}_3\text{H}_5$.

predicted. The computed EPR parameters of the Ni$^{\text{III}}$ precursor $\text{C}_3\text{H}_5$ (geometry shown in Figure 5.5b) are very different, showing a nearly axial g tensor and much smaller phosphorus hyperfine interactions, thus confirming that oxidation of Ni$^{\text{II}}$ complex $\text{C}_3\text{H}_5$ to Ni$^{\text{III}}$ complex $\text{C}_3\text{H}_5$ is followed by immediate C-C RE to form Ni$^{\text{II}}$ complex $\text{C}_3\text{H}_5$.

In an attempt to observe Ni$^{\text{III}}$ intermediate $\text{C}_3\text{H}_5$, EPR spectroelectrochemistry was carried out at low temperature but this did not result in any EPR signal. In another attempt, the chemical oxidation of $\text{C}_3\text{H}_5$ was carried out at -78 °C and transferred directly to a pre-cooled EPR tube. At 30 K, an EPR-signal different than that of $\text{C}_3\text{H}_5$ is present which converts to the EPR-signal of $\text{C}_3\text{H}_5$ when warmed up to RT for 5 minutes and remeasured at 30 K. The observation of a transient species that forms $\text{C}_3\text{H}_5$ at RT fits with the description of Ni$^{\text{III}}$ complex $\text{C}_3\text{H}_5$, however, the DFT-calculated g-values for $\text{C}_3\text{H}_5$ (Table 5.1) do not correspond at all with the found signal (see experimental section). Although the small coupling constants $A^\text{P}$ are nicely reproduced, according to the broadness of the signal, the calculated $g_z$-value of 2.02 is shifted to a higher g-value in the observed spectrum. This shift is unexpected for square pyramidal and octahedral d$^7$ complexes in which the unpaired electron resides in the d$_{z^2}$-orbital because spin-orbit coupling rules predict no mixing of the SOMO with other orbitals. This leads to an expected $g_z$ value around 2.0, which is commonly observed for other Ni$^{\text{III}}$ complexes. Consequently, it is unlikely that the observed EPR-signal originates form complex $\text{C}_3\text{H}_5$. Unfortunately, it is unclear at the moment what the exact species is.

Similar oxidation experiments were carried out for complex $\text{C}_3\text{F}_3$. Because complex $\text{C}_3\text{F}_3$ has an oxidation potential of 0.51 V, a stronger oxidant than [acetylferrocenium]$^+$ is required and [thianthrenium]$^+$ was used. Unfortunately, despite many attempts, a clear EPR signal was never observed for this reaction. It is known that (BOXAM)NiCF$_3$ complexes undergo homolytic bond splitting to form CF$_3$ radicals which was proven by
the addition of the spin trap \textit{N}-tert-butyl-\textalpha-phenylnitronitrile (PBN). When PBN reacts with CF$_3^\cdot$, a very characteristic EPR signal (triplet of quintets) is obtained with hyperfine-splitting to $^{14}$N and $^{19}$F. In the section on electrochemical experiments, it was already discussed that homolytic Ni-R bond cleavage is unlikely. To be sure that the absence of an EPR signal is not due to the formation of transient CF$_3$ radicals, the same spin trap was added. The characteristic triplet of quintets is not observed, but instead a doublet is detected in the RT EPR spectrum. It can be concluded that the CF$_3$-adduct is not formed because a signal for any spin-trap-adduct should consist of a triplet due to the hyperfine-splitting to $^{14}$N, but the origin of the doublet is still unknown.

Surprisingly, the same doublet could be observed without the addition of PBN suggesting the signal belongs to a persistent organic radical originating from oxidized 2CF$_3$. When the oxidation of 2CF$_3$ is carried out at -78 °C, immediately frozen in liquid N$_2$, and directly measured at 30 K, a signal for a Ni-centered radical is present (see experimental section). After the same sample is warmed to RT for a minute and then measured again at 30 K, the signal for a Ni-centered radical decayed and the doublet belonging to an organic radical appeared. This experiment shows that the product from oxidation of 2CF$_3$ is very unstable and decomposes to produce an organic radical that is not trapped with PBN. At the moment it is uncertain what the structure of the organic radical is.

The observation of a Ni$^\text{i}$ species after oxidation of 2CH$_3$ is a strong indication that C-C RE took place from Ni$^\text{iii}$ complex 4CH$_3$, but it is not conclusive proof. The detection of radical species by EPR does not give information about the purity of the sample. Moreover, for complex 2CF$_3$ we did not succeed to obtain an interpretable EPR signal. Therefore, we also studied the chemical oxidation by UV/Vis.

### Table 5.2: Experimental$^a$ and DFT calculated$^{b,c,d}$ EPR parameters of Ni$^\text{i}$ complex 5CH$_3$ and its Ni$^\text{iii}$ precursor 4CH$_3$.

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<td>$\rho^\text{Ni,e}$$^e$</td>
<td>-</td>
<td>0.74</td>
<td>0.83</td>
<td></td>
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$^a$ Values obtained by spectral simulation.
$^b$ Optimized with Turbomole (BP86, def2-TZVP, disp3).
$^c$ Orca (b3-lyp, def2-TZVP).
$^d$ ADF (B3LYP, TZ2P), SOC, ZORA, unrestricted, collinear.
$^e$ Atomic spin populations (Turbomole, BP86, def2-TZVP, disp3).
Upon addition of one equivalent of [ferrocenium]PF₆ to a solution of complex 2CH₃, a similar transition is observed in the UV/Vis spectrum as for the electrochemical oxidation. The bands at λ 452 nm and 241 nm disappear upon oxidation and the band that appears at λ 278 nm could belong to NiI complex 5MeI (Figure 5.6a).

Figure 5.6: (a) UV/Vis spectra of complex 2CH₃ (red) and after oxidation by 1 equivalent FcPF₂ (blue). (b) UV/Vis spectra of complex 2CH₃ (red), after oxidation by 1 equivalent of AgBF₄ (black), and after oxidation by 2 equivalents of AgBF₄ (blue).

AgBF₄ can also be used as an oxidant and when one equivalent of AgBF₄ is added to a MeCN solution of 2CH₃, a precipitation is observed within five minutes, indicating the formation of Ag⁰ particles. Surprisingly, UV/Vis spectroscopy shows that still ±50% of starting material is present after filtration and that full conversion can be reached with two equivalents of AgBF₄ (Figure 5.6). The obtained product has one characteristic band at λ 279 nm, which is again similar to the product from spectroelectrochemistry (Figure 5.3). These results suggest that the reductive elimination and the second oxidation from NiI 5CH₃ to NiII (C) are both fast; at least faster than the oxidation of complex 2CH₃ to NiIII. However, it was proven by NMR spectroscopy and mass spectrometry that a different reaction occurs in the case of Ag⁰.

Although the NiII product (C) is expected to be tetrahedral and therefore paramagnetic, the product of the reaction of 2CH₃ with two equivalents of AgBF₄ is diamagnetic and shows a well-defined ¹H NMR spectrum with a signal at δ 2.26 ppm that is assigned to the Ph-CH₃ group. This is the first solid evidence that reductive C₆H₅-CH₃ coupling occurred. Furthermore, the aromatic region shows typical signals for a freely rotating phenyl-group, instead of a cyclometalated one, that integrates for four protons. The ³¹P NMR spectrum shows two doublets around δ 140 ppm (plus another similar side product) which is an unlikely signal for the putative NiII product but fits with a Ag¹ complex. Silver has two stable isotopes, ¹⁰⁷Ag and ¹⁰⁹Ag, which both have a nuclear spin of ½ and have almost equal natural abundance. Accordingly, the signal in ³¹P NMR can now be described as two overlapping doublets at δ 139.12 ppm, ¹⁰⁷Ag·P = 707 Hz and ¹⁰⁹Ag·P = 618 Hz. The broadening of the signals is caused by fast dissociation/association of the phosphine. Based on a very similar complex from literature, a dimeric structure
Figure 5.7: (a) $^1$H NMR spectrum in MeCN-d$_3$ from the reaction of complex $2^{\text{CH}_3}$ with two equivalents of AgBF$_4$ and (b) corresponding $^{31}$P NMR spectrum. (c) $^{31}$P NMR spectrum in MeCN-d$_3$ from the reaction of complex $2^{\text{CF}_3}$ with one equivalent of [thianthrenium]BF$_4$ and one equivalent of AgBF$_4$ and (d) corresponding $^{19}$F NMR spectrum.

is proposed for complex $6^{\text{CH}_3}$ (Scheme 5.6). Furthermore, a molecular ion peak for a mononuclear MeCN-adduct was found with HRMS (CSI) at $m/z$ 477.1248, confirming the formation of complex $6^{\text{CH}_3}$. These results explain why two equivalents of AgBF$_4$ are necessary for complete conversion of $2^{\text{CH}_3}$; complex $5^{\text{CH}_3}$ is very unstable in the presence of Ag$^+$ and the Ni$^{1+}$-center is rapidly replaced by Ag$^+$. Although attempts to produce single crystals of $6^{\text{CH}_3}$ were unsuccessful, it was possible to isolate single crystals of [Ni$^{1+}$(MeCN)$_6$](BF$_4$)$_2$ from the reaction mixture. The crystal structure showed that the Ni-center is divalent, which could be explained by the disproportionation of unstable [Ni$^{1+}$(MeCN)$_6$]BF$_4$ into Ni$^{0}$ and [Ni$^{1+}$(MeCN)$_6$](BF$_4$)$_2$.

Reconsidering the UV/Vis spectrum from complex $6^{\text{CH}_3}$ (Figure 5.6), it is peculiar that a similar spectrum is obtained after oxidation with spectroelectrochemistry, be-
cause the product from spectroelectrochemistry can intuitively not contain Ag\(^{I}\). However, it is possible that the similarity between both UV/Vis spectra is just coincidence or that the band at \(\lambda\) 277 nm belongs to an intraligand (\(\pi-\pi^*\)) transition and is similar for both Ag\(^{I}\) and Ni\(^{II}\)/Ni\(^{III}\) complexes.

As it seems that Ag\(^{I}\) can be used as an effective scavenger for the unstable Ni\(^{I}\) complex, this method was also applied for complex 2\(^{CF_3}\) [Scheme 5.6]. Although the oxidizing potential of AgBF\(_4\) in CH\(_2\)Cl\(_2\) should be strong enough for the oxidation of 2\(^{CF_3}\), no reaction occurred in this solvent. Therefore, the reaction was carried out with [thianthrenium]BF\(_4\) in MeCN-d\(_3\) in the presence of AgBF\(_4\). Directly after addition, \(^{31}\)P NMR showed that a product similar to 6\(^{CH_3}\) is formed and in \(^{19}\)F NMR a signal is observed at \(\delta\) -57 ppm, exactly where it is expected for the product after C\(_{Ph}\)-CF\(_3\) RE. \(^{31}\)HRMS (CSI) also confirmed in this case that Ag\(^{I}\) complex 6\(^{CF_3}\) was formed (\(m/z\) 531.0953). This data strongly support that oxidation of complex 2\(^{CF_3}\) was followed by RE resulting in C-CF\(_3\) coupling. The group of Klein has previously reported that cyclometalated (Phbpy)Ni\(^{III}\)CF\(_3\) complexes are not stable in solution and undergo C\(_{Ph}\)-CF\(_3\) coupling,\(^{32}\) but this is the first time that such facile C\(_{Ph}\)-CF\(_3\) RE from a Ni\(^{III}\) species is observed. C-CF\(_3\) coupling from other Ni complexes require longer reaction times and higher temperatures.\(^{8,15}\)

## 5.2.5 Reduction

To provide a full description of the electrochemical behaviour of cyclometalated Ni\(^{III}\)-alkyl complexes, the reduction was also investigated, which could hypothetically produce a Ni\(^{I}\)-complex. Compared to Ni\(^{I}\)-complex 5\(^{CH_3}\) having only \(P,N\)-ligand coordination, we wondered what kind of influence the bonding of the phenyl moiety to Ni would have on the spectroscopic features.

The cyclic voltammograms of 2\(^{CH_3}\) and 2\(^{CF_3}\) show a reversible reduction wave at \(E_{1/2}\) -2.60 V and -2.36 V, respectively [Figure 5.8]. The observed difference in reduction potentials of 2\(^{CH_3}\) and 2\(^{CF_3}\) is in agreement with the DFT calculations, which predicted that the reduction of 2\(^{CF_3}\) would occur at a higher potential due to stabilization of the LUMO by the CF\(_3\) ligand. Both processes seem to be reversible at the scan speed of 100 mV/s, although the wave of 2\(^{CF_3}\) has a small shoulder which is most likely a small impurity.

Spectroelectrochemistry was performed in THF, in which both complexes show similar behaviour. The reduction event of 2\(^{CH_3}\) occurs at such negative potential that the solvent interfered with the measurement. This problem is not observed for 2\(^{CF_3}\).
and upon spectroelectrochemical reduction, three new broad and partially structured band systems in the NIR and vis region with maxima at $\lambda$ 1090, 661 and 430 nm appeared, and one intense new band in the UV at $\lambda$ 324 nm, while the initial bands at $\lambda$ 393 and 343 nm are either shifted to higher energy or vanish (Figure 5.9). The very intense band at $\lambda$ 245 nm is reduced in intensity to about 50%. The reduction event is reversible for a time period up to 20 minutes. These features are reminiscent of the ligand-centered reduction of bipyridine-complexes and indicate a reduction centered at the phenylpyridine core of the ligand of $2\text{CF}_3$ rather than on the Ni center.

To prove that the reduction is ligand centered, complex $2\text{CH}_3$ and $2\text{CF}_3$ were reacted with KC$_8$ in THF (Figure 5.10a), which caused a slight darkening of the solutions. The EPR spectrum of compound $7\text{CH}_3$ measured in isotropic solution reveals a set of well-resolved hyperfine couplings (Figure 5.10). The spectrum is characteristic for a ligand radical complex. A satisfactory simulation was obtained with the parameters shown in Table 5.3. The DFT computed EPR parameters are in agreement with the experimental data (Table 5.3b). The DFT computed electronic structure of $7\text{CH}_3$ reveals a mainly ligand-centred spin density distribution. The SOMO and spin density plots of $7\text{CH}_3$ are shown in Figure 5.11. For complex $7\text{CF}_3$ a similar signal is observed in EPR, although the hyperfine splitting is less resolved and the intensity of the signal is much lower (see...
Figure 5.10: (a) Reaction of $^{2}$CH$_3$ and $^{2}$CF$_3$ with the reductant KC$_8$ to produce anionic complexes $^{7}$CH$_3$ and $^{7}$CF$_3$ (b) Experimental and simulated X-band EPR spectra of Ni$^{II}$-ligand radical complex $^{7}$CH$_3$ measured in isotropic solution (THF) at RT. Experimental conditions: Temperature = 298 K, microwave power 2.0 mW, field modulation amplitude = 1 Gauss, microwave frequency = 9.390764 GHz. The simulated spectrum was obtained with the parameters shown in Table 5.3.

Figure 5.11: SOMO (a) and spin density plot (b) of complex $^{7}$CH$_3$ (Turbomole, BP86, def2-TZVP)
5.3 Conclusions

In this Chapter, we report our study on \( \text{C}_{\text{sp}^2}-\text{C}_{\text{sp}^3} \) reductive elimination from cyclometalated Ni\( ^{\text{III}} \) complexes. For this purpose, complexes \( 2\text{CH}_3 \) and \( 2\text{CF}_3 \) were designed bearing the cyclometalated PNOC\( _\text{Ph} \)-ligand and an additional -CH\( _3 \) and -CF\( _3 \) group, respectively. Complex \( 2\text{CH}_3 \) was expected to undergo facile RE after oxidation, while \( 2\text{CF}_3 \) was supposed to be stable in the higher oxidation state due to the known reluctance to RE of the -CF\( _3 \) group.

Surprisingly, it was shown that \( 2\text{CH}_3 \) and \( 2\text{CF}_3 \) possess similar electrochemical behaviour in cyclic voltammetry en UV/Vis spectroelectrochemistry. Both oxidations are completely irreversible and both products show similar features in UV/Vis. Chemical oxidation of \( 2\text{CH}_3 \) with [acetylferrocenium]BF\( _4 \) resulted in an EPR signal that was attributed to tetrahedral Ni\( ^{\text{I}} \) complex \( 5\text{CH}_3 \), suggesting that RE occurred after the oxidation to Ni\( ^{\text{III}} \). Attempts to observe the Ni\( ^{\text{III}} \) intermediate by performing the oxidation at low temperature did not result in EPR signals that could be assigned. Furthermore, EPR experiments on the oxidized product from \( 2\text{CF}_3 \) did not yield any interpretable signals.

It was discovered that Ag\( ^1 \) can be used as a scavenger for the unstable and paramagnetic Ni\( ^{\text{I}} \) complexes for both \( 2\text{CH}_3 \) and \( 2\text{CF}_3 \). The resulting Ag\( ^1 \) complexes \( 6\text{CH}_3 \) and \( 6\text{CF}_3 \) are diamagnetic and NMR studies strongly suggest that C-C reductive elimination occurred for both complexes. Complexes \( 6\text{CH}_3 \) and \( 6\text{CF}_3 \) are formed instantaneous upon the addition of oxidant in the presence of AgBF\( _4 \) at RT. Such facile RE is especially remarkable for \( 2\text{CF}_3 \) and is unprecedented to occur from Ni\( ^{\text{III}} \) complexes.

The results presented in this Chapter support that C-C bond formation can be induced by oxidation of cyclometalated Ni\( ^{\text{III}} \) complexes. RE seems to be very fast, also
for the challenging C-CF₃ coupling. This discovery opens up possibilities to develop Ni-catalyzed trifluoromethylation reactions that are based on C-H activation.

In addition to the investigation on oxidation of 2CH₃ and 2CF₃, the reversible reduction of these complexes is reported. Both spectroelectrochemistry and EPR point out that it is possible to reduce the phenylpyridine core of the ligand to produce a ligand-centered radical.

Acknowledgements

Bas de Bruin is thanked for the DFT and TD-DFT calculations. René Becker and Riccardo Zaffaroni are thanked for their help with electrochemistry. Prof. Axel Klein, Nicolas Vogt and Aaron Sandleben are thanked for their work on spectroelectrochemistry experiments on the reduction of complex 2CF₃ and for discussions on electrochemistry. Prof. František Hartl is thanked as well for discussions on these topics. Christophe Rebreyend is thanked for his help with EPR measurements.

5.4 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. The synthesis of complex 1 is described in Chapter 3. THF, pentane, hexane and Et₂O were distilled from sodium benzophenone ketyl, CH₂Cl₂ was distilled from CaH₂, toluene from sodium under nitrogen. NMR spectra (¹H, ³¹P, and ¹³C{¹H}) were measured on a Bruker DRX 500, Bruker AV 400, Bruker DRX 300 or on a Bruker AV 300 spectrometer. A Shimadzu UV 2700 spectrophotometer was used to record UV/vis spectra. High resolution mass spectra were recorded on a JMS-T100GCV mass spectrometer using field desorption (FD), or JEOL AccuTOF LC, JMS-T100LP mass spectrometer using electron-spray ionization (ESI or CSI). Elemental analyses were carried out by Mikroanalytisches Laboratorium Kolbe.

Diffusion ordered NMR spectroscopy (DOSY) was used to determine the diffusion coefficients of complexes 2CH₃ and 2CF₃. The spectra were measured on a Bruker DRX 300 with temperature and gradient calibration. The temperature was controlled at 298 K during the measurements. The parameters that were used are: δ = 1200 μs (p30), Δ = 0.2 s (d20).

Synthesis of Ni(CH₃)(κ-³-P,N,C-1-O) (2CH₃). Complex 1 (0.080 g, 0.18 mmol) was dissolved in toluene (5 mL) and MeLi (1.6 M in Et₂O) (110 μL, 0.18 mmol) was added, resulting in a color change from orange to red. After 5 min stirring, the suspension was filtered over Celite and the solvent evaporated. The product was extracted with pentane (15 mL), filtered and dried in vacuo to yield 2CH₃ as a bright orange solid (0.055 g, 80%). Crystals suitable for X-ray analysis were grown by slow evaporation of an Et₂O solution. ¹H NMR (300 MHz, MeCN-d₃, ppm): δ 7.77 (vt, J = 7.9 Hz, 1H, Py-CH), 7.51 (dt, J = 7.5, 1.7 Hz, 1H, Ph-CH), 7.46-7.37 (m, 1H, Ph-CH), 7.32 (dd, J = 7.7, 0.8 Hz, 1H, Py-CH), 7.20 (tt, J = 7.3, 1.7 Hz, 1H, Ph-CH), 7.04 (td, J = 7.4, 1.4 Hz, 1H, Ph-CH), 6.80
(d, J = 8.2 Hz, 1H, Py-CH), 1.41 (d, 3J_{HP} = 13.6 Hz, 18H, (CH$_3$)$_3$CP), -0.06 (d, 3J_{HP} = 9.1 Hz, 3H, Ni-CH$_3$). $^{31}$P NMR (121 MHz, MeCN-d$_3$, ppm): δ 194.28. $^{13}$C NMR (75 MHz, MeCN-d$_3$, ppm): textdelta 165.74 (d, 2J$_{CP}$ = 92.2 Hz, Ni-C), 164.73 (d, J$_{CP}$ = 4.5 Hz, Py-C), 164.01 (d, J$_{CP}$ = 9.5 Hz, Py-C), 150.28 (s, Ph-C), 141.79 (s, Py-CH), 134.37 (s, Ph-CH), 130.21 (d, J$_{CP}$ = 5.3 Hz, Ph-CH), 125.09 (s, Ph-CH), 123.09 (d, J$_{CP}$ = 3.5 Hz, Ph-CH), 111.62 (s, Py-CH), 107.11 (d, J$_{CP}$ = 4.0 Hz, Py-CH), 39.16 (d, J$_{CP}$ = 4.2 Hz, (CH$_3$)$_3$CP), 27.82 (d, J$_{CP}$ = 6.8 Hz, (CH$_3$)$_3$CP), -10.92 (d, J$_{CP}$ = 14.7 Hz, Ni-CH$_3$). DOSY (MeCN-d$_3$, 25°C): log D = -8.76 m$^2$/s. HRMS: compound was too unstable, only mass of oxidized methylated ligand was found. UV/Vis: λ 241 (ε = 1.7·10$^4$ L·mol$^{-1}$·cm$^{-1}$), λ 313 (ε = 7.8·10$^3$ L·mol$^{-1}$·cm$^{-1}$), λ 452 (ε = 1.3·10$^3$ L·mol$^{-1}$·cm$^{-1}$).

Synthesis of Ni(CF$_3$)(κ$^3$-P,N,C-I-O) (2CF$_3$). THF (10 mL) was added to a Schlenk containing complex 1 (0.080 g, 0.18 mmol) and CsF (0.080 g, 0.53 mmol). After stirring for 20 min, TMS-CF$_3$ (2.0 M in THF) (0.27 mL, 0.53 mmol) was added dropwise and the reaction was stirred overnight. Subsequently, more TMS-CF$_3$ (0.13 mL, 0.27 mmol) was added and the reaction was stirred for an additional 4 hours. THF was evaporated and the product was extracted with pentane. After filtration the solvent was evaporated to yield 2CF$_3$ as a yellow solid (0.078 g, quantitative). Crystals suitable for X-ray analysis were grown by slow evaporation of an Et$_2$O solution. $^1$H NMR (300 MHz, MeCN-d$_3$, ppm): δ 7.84 (vt, J = 8.0 Hz, 1H, Py-CH), 7.56-7.43 (m, 2H, Py-CH), 7.34 (d, J = 7.7 Hz, 1H, Py-CH), 7.20-7.04 (m, 2H, Ph-CH), 6.82 (d, J = 8.2 Hz, 1H, Py-CH), 1.45 (d, 3J$_{HP}$ = 14.2 Hz, 18H, (CH$_3$)$_3$CP). $^{31}$P NMR (121 MHz, MeCN-d$_3$): δ 194.96 (q, 3J$_{PF}$ = 25.8 Hz). $^{19}$F NMR(282 MHz, MeCN-d$_3$, ppm): δ -10.93 (d, 3J$_{FP}$ = 25.6 Hz). $^{13}$C NMR(126 MHz, MeCN-d$_3$, ppm): δ 165.69 (d, J$_{CP}$ = 3.6 Hz, Py-C), 164.34 (d, J$_{CP}$ = 9.3 Hz, Py-C), 161.60 (dq, 2J$_{CP}$ = 82.5 Hz, 3J$_{CF}$ = 3.2 Hz, Ni-C), 149.31 (s, Ph-C), 144.55 (s, Ph-C), 143.51 (qd, 1J$_{CF}$ = 357 Hz, 2J$_{CP}$ = 18.4 Hz, NiCF$_3$), 139.83 (m, Ph-CH), 130.83 (d, J$_{CP}$ = 5.9 Hz, Ph-CH), 126.24 (s, Ph-CH), 123.34 (d, J$_{CP}$ = 3.2 Hz, Ph-CH), 112.24 (s, Ph-CH), 108.06 (d, J$_{CP}$ = 3.8 Hz, Ph-C), 39.23 (d, J$_{CP}$ = 4.9 Hz, (CH$_3$)$_3$CP), 27.79 (d, 2J$_{CP}$ = 6.5 Hz, (CH$_3$)$_3$CP). DOSY (MeCN-d$_3$, 25°C): log D = -8.77 m$^2$/s. HRMS (ESI): m/z calcd. for C$_{20}$H$_{25}$F$_3$NiO: 442.1058 [M]$^+$; found: 442.1077.

UV/Vis (nm): λ 245 (ε = 2.6·10$^4$ L·mol$^{-1}$·cm$^{-1}$), λ 304 (ε = 5.8·10$^3$ L·mol$^{-1}$·cm$^{-1}$), λ 331 (ε = 4.5·10$^3$ L·mol$^{-1}$·cm$^{-1}$), λ 340 (ε = 5.3·10$^3$ L·mol$^{-1}$·cm$^{-1}$), λ 395 (ε = 1.3·10$^3$ L·mol$^{-1}$·cm$^{-1}$).

Synthesis of complex Ni(MeCN)(κ$^3$-P,N,C-I-O)BF$_4$ (3). Complex 1 (20 mg, 0.044 mmol) was dissolved in MeCN (2) and AgBF$_4$ (8.6 mg, 0.044 mmol) was added. After stirring for 30 min., the reaction was filtered over Celite and the solvent was evaporated. Complex 6$^{6}$CH$_3$ was obtained as yellow solid (22 mg, quantitative). $^1$H NMR(500 MHz, MeCN-d$_3$, ppm): δ 7.96 (vt, J = 8.0 Hz, 1H, Py-CH), 7.50-7.46 (m, 1H, Ph-CH), 7.41 (dd, J = 7.7, 1.0 Hz, 1H, Py-CH), 7.25-7.18 (m, 2H, Ph-CH), 7.15-7.10 (m, 1H, Ph-CH), 6.90 (dd, J = 8.3, 1.0 Hz, 1H, Py-CH), 1.50 (d, 3J$_{HP}$ = 15.2 Hz, 18H, (CH$_3$)$_3$CP). $^{31}$P NMR(121 MHz, MeCN-d$_3$, ppm): δ 190.17. $^{13}$C NMR(126 MHz, MeCN-d$_3$, ppm): δ 167.67 (d, J$_{CP}$ = 3.3 Hz, Py-C), 165.45 (d, J$_{CP}$ = 9.6 Hz, Py-C), 155.60 (d, 2J$_{CP}$ = 86.4 Hz, Ni-C), 148.49 (s, Ph-C), 146.09 (s, Py-CH), 135.05 (s, Ph-CH), 131.50 (d, J$_{CP}$ = 6.4 Hz, Ph-CH), 128.07 (s, Ph-CH), 124.24 (d, J$_{CP}$ = 3.6 Hz, Ph-C), 113.76 (s, Ph-C), 109.53 (d, J$_{CP}$ = 4.4 Hz, Py-C), 39.71 (d, J$_{CP}$ = 6.0 Hz, (CH$_3$)$_3$CP), 27.26 (d, 2J$_{CP}$ = 6.4 Hz, (CH$_3$)$_3$CP). HRMS (ESI): m/z calcd. for C$_{21}$H$_{28}$N$_2$NiO: 413.1293 [M]$^+$; found: 413.1290. UV/Vis (MeCN, nm): λ 241 (ε = 2.0·10$^4$ L·mol$^{-1}$·cm$^{-1}$), λ 271 (ε = 3.5·10$^4$ L·mol$^{-1}$·cm$^{-1}$), λ 307 (ε = 7.1·10$^3$ L·mol$^{-1}$·cm$^{-1}$), λ 340 (ε = 1.3·10$^3$ L·mol$^{-1}$·cm$^{-1}$).
Synthesis of complex \( \text{6CH}_3 \). To a Schlenk containing complex \( \text{2CH}_3 \) (10 mg, 0.026 mmol) and \( \text{AgBF}_4 \) (10 mg, 0.052 mmol) was added MeCN (2 mL). The reaction was stirred for 5 minutes after which it was filtered and evaporated to dryness. As the product could not be separated from the nickel-containing by-products, complex \( \text{6CH}_3 \) was only characterized in situ.

\( ^1\text{H} \) NMR (300 MHz, MeCN-d3, ppm): \( \delta 7.92 (t, J = 7.8 \text{ Hz}, 1\text{H}), 7.35 (m, 4\text{H}), 7.22 (d, J = 5.2 \text{ Hz}, 1\text{H}), 7.03 (d, J = 8.0 \text{ Hz}, 1\text{H}), 2.26 (s, 3\text{H, Ph-CH}_3), 1.25 (d, J = 15.4 \text{ Hz}, 18\text{H, (CH}_3)_3\text{CP}) \). 

\( ^{31}\text{P} \) NMR (121 MHz, MeCN-d3, ppm): \( \delta 139.12 \) (dd, \( J_{\text{P-107Ag}} = 707 \text{ Hz}, J_{\text{P-109Ag}} = 618 \text{ Hz} \)). 

\( ^{13}\text{C} \) NMR (75 MHz, MeCN-d3, ppm): \( \delta 162.30 \) (s, Py-C), 158.20 (m, Py-C), 142.32 (s, Py-CH), 140.83 (s, Ph-C), 136.56 (s, Ph-C), 131.27 (s, Ph-CH), 130.36 (s, Ph-CH), 129.64 (s, Ph-CH), 112.31 (s, Py-CH), 37.58-36.58 (m, (CH\(_3\))\(_3\)CP), 27.16 (d, \( J_{\text{CP}} = 10.9 \text{ Hz}, (\text{CH}_3)_3\text{CP} \)). One of the Py-CH signal falls under the solvent residual signal. HRMS (CSI): \( m/z \) calcd. for C\(_{22}\)H\(_{31}\)AgN\(_2\)OP: 477.1225 [M]+; found: 477.1248.

Synthesis of complex \( \text{6CF}_3 \). To a Schlenk containing complex \( \text{2CF}_3 \) (10 mg, 0.023 mmol), [thianthrenium]BF\(_4\) (7.0 mg, 0.023 mmol) and AgBF\(_4\) (4.4 mg, 0.023 mmol) was added MeCN (2 mL). The reaction was stirred for 5 minutes, after which it was filtered and evaporated to dryness. As the product could not be separated from the Ni-containing by-products and thianthrene, the product was only characterized in situ.

\( ^1\text{H} \) NMR (300 MHz, MeCN-d3, ppm): \( \delta 8.00-7.67 (m, 4\text{H, Py-CH and 3 Ph-CH}), 7.55 (\text{thianthrene and 1 Ph-CH}), 7.33 (\text{m, thianthrene}), 7.25 (d, J = 7.38 \text{ Hz, Py-CH}), 7.12 (d, J = 8.30, Py-CH), 1.24 (d, J = 15.5 \text{ Hz, (CH}_3)_3\text{CP}) \). 

\( ^{19}\text{F} \) NMR (282 MHz, MeCN-d3, ppm): \( \delta -57.25 (\text{s, Ph-CF}_3), -151.76 (\text{s, BF}_4) \). HRMS (CSI): \( m/z \) calcd. for C\(_{22}\)H\(_{28}\)AgF\(_3\)N\(_2\)OP: 531.0942 [M]+; found: 531.0953.

**Electrochemistry:** All cyclic voltammograms are measured in PrCN with [tetrabutylammonium]PF\(_6\) (0.1 M) as the supporting electrolyte. Concentration of the analyte: 6 mM. Working electrode: glassy carbon. Counterelectrode: Pt coil. Reference-electrode: Ag coil. Scanspeed: 100 mV s\(^{-1}\). All redox potentials are referenced to Fc/Fc\(^+\).

**Spectroelectrochemistry:** UV/Vis spectra were measured with an OTTLE cell. The oxidation measurements were carried out in MeCN with [tetrabutylammonium]PF\(_6\) (0.2 M) as the supporting electrolyte. Working electrode: Pt. Counterelectrode: Pt. Reference-electrode: Ag-wire. Scan speed: 0.003 V s\(^{-1}\). The reduction measurements were carried out in THF.

**EPR spectroscopy.** Experimental X-band EPR spectra were recorded on a Bruker EMX spectrometer (Bruker BioSpin Rheinstetten) equipped with a He temperature control cryostat system (Oxford Instruments). Simulations of the EPR spectra were performed by iteration of the anisotropic g-values and line widths using the EPR simulation program W95EPR developed by Prof. Dr. Frank Neese.

**Oxidation of 2\( \text{CH}_3 \):** A solution of [acetylferrocenium]BF\(_4\) (13 \( \mu \)mol, 4.1 mg) in a mixture of PrCN/MeCN = 3:1 (0.2 mL) was added to a solution of complex 2\( \text{CH}_3 \) (13 \( \mu \)mol, 5.0
mg) in the same solvent (0.2 mL) in the glovebox. 0.2 mL of the reaction mixture was transferred directly to an EPR tube and the sample was frozen in liquid N$_2$ as fast as possible. At low temperature: sample was prepared outside the glovebox with at -78 °C and precooled solutions and EPR tube. The sample was directly frozen in liquid N$_2$.

Oxidation of 2$^{\text{CF}_3}$: A solution of [thianthrenium]BF$_4$ (11 μmol, 3.2 mg) in a mixture of PrCN/MeCN = 3:1 (0.2 mL) was added to a solution of complex 2$^{\text{CF}_3}$ (11 μmol, 5.0 mg) in the same solvent (0.2 mL) in the glovebox. 0.2 mL of the reaction mixture was transferred directly to an EPR tube and the sample was frozen in liquid N$_2$ as fast as possible. At low temperature: sample was prepared outside the glovebox with at -78 °C and precooled solutions and EPR tube. The sample was directly frozen in liquid N$_2$.

Reduction of 2$^{\text{CH}_3}$: KC$_8$ (13 μmol, 1.8 mg) was added to a solution of 2$^{\text{CH}_3}$ (13 μmol, 5.0 mg) in THF (0.4 mL) and the reaction was stirred for 90 minutes at RT. The reaction mixture is filtered and 0.2 mL was transferred to a capillary inside an EPR tube.

Reduction of 2$^{\text{CF}_3}$: KC$_8$ (11 μmol, 1.5 mg) was added to a solution of 2$^{\text{CF}_3}$ (11 μmol, 5.0 mg) in THF (0.4 mL) and the reaction was stirred for 90 minutes at RT. The reaction mixture was filtered and 0.2 mL was transferred to a capillary inside an EPR tube.

**Computational details and EPR property calculations.** Geometry optimizations were carried out with the Turbomole program package coupled to the PQS Baker optimizer via the BOpt package at the ri-DFT/BP86 level. We used Grimme’s D3 dispersion corrections (disp3) and the def2-TZVP basis set for all atoms, and a small grid (m4). EPR parameters were subsequently calculated with the ADF program system at the B3LYP/TZ2P level, using the coordinates from the structures optimized in Turbomole as input. ZORA basis sets as supplied with the ADF program were used, employing unrestricted SPINORBIT ZORA COLLINEAR calculations for the SOC corrected HFI-tensors and Zeeman corrected g-tensors. EPR parameters were also calculated with the ORCA program package (version 3.0.3.), again using the coordinates from the structures optimized in Turbomole as input, now employing the b3-lyp functional and the def2 TZVP basis set.
Figure 5.13: (a) EPR spectrum at 30 K of the reaction of $^{2}\text{CH}_3$ with [acetylferrocenium]BF$_4$ carried out at -78°C in PrCN/MeCN = 3:1. (b) EPR spectrum at 30K after warming the EPR tube to RT. (c) EPR spectrum at 30K of the reaction of $^{2}\text{CF}_3$ with [thianthrenium]BF$_4$ carried out at -78°C in PrCN/MeCN = 3:1. (d) EPR spectrum at 30K after warming the EPR tube to RT.

Figure 5.14: Experimental X-band EPR signal of $^{7}\text{CF}_3$ in isotropic solution (THF) at RT. Experimental conditions: Temperature: 298 K, microwave power 20.0 mW, field modulation amplitude = 1 Gauss, microwave frequency 9.390819 GHz.
C-C bond formation from Ni$^{III}$ complexes

TD-DFT calculations. The UV/Vis transitions of complex 2$^{\text{CH}_3}$ intermediates A/4$^{\text{CH}_3}$ and C were calculated with TD-DFT (nroots = 50; maxdim = 600; triplets = false) as implemented in the ORCA package at the b3-lyp level (RIJ/COSX) using the def2-TZVP basis set. ZORA scalar relativistic Hamiltonians (Special-GridAtoms = 27, SpecialGridIntAcc = 7) and COSMO delectric solvent corrections (\(\epsilon = 37.5; \text{MeCN}\)) were included. The coordinates from the structures optimized in Turbomole were used as input for these ORCA TD-DFT calculations.

X-ray crystallography studies. X-ray intensities were measured on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator (\(\lambda = 0.71073 \text{ Å}\)) 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 located in difference Fourier maps. Metal bound hydrogen atoms H1 in complex 4-CH$_2$ and 4-O were refined freely with an isotropic displacement parameter, all other hydrogen atoms were refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.

For 2$^{\text{CH}_3}$: C$_{20}$H$_{29}$NiOP, Fw = 388.11, T = 150 K, orange plate, 0.197×0.221×0.431 mm$^3$, monoclinic, C 2/c (no. 15), a = 43.970(3), b = 14.3860(10), c = 24.9872(16) Å, \(\beta = 94.791(7)^\circ\), \(V = 15750.5 \text{ Å}^3\), \(Z = 34\), \(D_x = 1.390 \text{ g cm}^{-3}\), \(\mu = 1.140 \text{ mm}^{-1}\). 221290 Reflections were measured up to a resolution of (sin \(\theta/\lambda\))$_{\text{max}}$ = 0.993 Å$^{-1}$. 14101 Reflections were unique (\(R_{\text{int}} = 0.1805\)), of which 9722 were observed \([I>2\sigma(I)]\). 893 Parameters were refined with no restraints. \(R_1/\sigma R_2\) \([I>2\sigma(I)]\): 0.0430/0.1084. \(R_1/\sigma R_2\) \([\text{all refl.}]\): 0.0835/0.1331. \(S = 0.848\). Residual electron density found between -0.36 and 0.44 e/Å$^3$.

Selected bond lengths [Å] and angles [°] for the other three independent molecules found in the unit cell of 2$^{\text{CH}_3}$: Ni2: Ni2 C12B 1.943(4); Ni2 C1B 1.933(4); Ni2 N1B 1.910(3); Ni2 N1P 2.161(1); C1B Ni2 N1B 83.9(2); C1B Ni2 C12B 92.4(2); C12B Ni2 N1B 83.3(2); C12B Ni2 P1A 166.9(1). For Ni3: Ni3 C12C 1.957(4); Ni3 C1C 1.939(4); Ni3 N1C 1.916(3); Ni3 P1C 2.173(1); C1C Ni3 N1C 83.6(2); C1C Ni3 C12C 93.2(2); C12C Ni3 P1C 100.2(1); P1C Ni3 N1C 82.68(9); C1C Ni3 P1C 166.1(1). For Ni4: Ni4 C12D 1.958(4); Ni4 C1D 1.939(4); Ni4 C1D 1.939(4); Ni4 P1D 2.162(1); C1D Ni4 N1D 84.0(1); C1D Ni4 C12D 93.4(2); C12D Ni4 P1D 99.8(1); P1D Ni4 N1D 82.88(9); C1D Ni4 P1D 166.9(1). For 2$^{\text{CF}_3}$: Ni1-C20 1.878(3); Ni1-C1 1.944(3); Ni1-N1 1.906(2); Ni1-P1 2.213(1); Ni1-N1-C1 84.3(1); C20-Ni1-C1 92.8(1); P1-Ni1-N1 82.69(9); P1-Ni1-C20 100.4(1); C1-Ni1-P1 166.1(1).

For 2$^{\text{CF}_3}$: C$_{20}$H$_{25}$F$_3$NiOP, Fw = 442.08, T = 150 K, yellow plate, 0.106×0.162×0.335 mm$^3$, monoclinic, P 2$_1$ 2$_1$ 2$_1$ (no. 19), a = 8.1987(10), b = 10.5103(13), c = 23.341(3) Å, \(V = 2011.31 \text{ Å}^3\), \(Z = 4\), \(D_x = 1.460 \text{ g cm}^{-3}\), \(\mu = 1.080 \text{ mm}^{-1}\). 40175 Reflections were measured up to a resolution of (sin \(\theta/\lambda\))$_{\text{max}}$ = 0.988 Å$^{-1}$. 5061 Reflections were unique (\(R_{\text{int}} = 0.0825\)), of which 3840 were observed \([I>2\sigma(I)]\). 250 Parameters were refined with no restraints. \(R_1/\sigma R_2\) \([I>2\sigma(I)]\): 0.0428/0.0617. \(R_1/\sigma R_2\) \([\text{all refl.}]\): 0.0824/0.0690.
References

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