Introduction

Nickel–alkyl species have become relevant for a wide variety of C–C bond-forming reactions, including Negishi, Suzuki–Miya-ura, Stille, Kumada and Hiyama couplings. The trifluoromethylation of arenes is industrially interesting because of the intriguing properties of fluoroorganic materials. In late transition metal complexes, the CF₃ substituent is usually strongly bound to the metal center and is therefore often not susceptible to reductive elimination. It was proposed that Ni could be an active catalyst for this transformation and the precise understanding of Ni–CF₃ bonding and reactivity of these complexes has been subject to several studies, usually in comparison to Ni–CH₃ bonding. The main findings show that the lone pair of the carbanionic CF₃ ligand has increased C 2s character and a stronger donation to the metal compared to the methyl analog. Furthermore, complexes with a CF₃ ligand usually show higher oxidation potentials compared to the corresponding CH₃ complexes.

Most previously reported mechanistic investigations and model systems for C–C coupling at Ni focus on cross-coupling reactions, in which the target phenyl ligand can freely rotate around the M–Ph bond. A recent model system that has proven very useful in this context is based on NiN′-di-tert-butyl-2,11-diaza[3,3](2,6)pyridinophane as ligand (Scheme 1A). We herein report complexes with a cyclometalated NiII center, in which the rotation of the phenyl ligand is constrained by the linkage to the adjacent pyridine moiety (Scheme 1B). These species can be regarded as model systems for the recently reported Ni-catalyzed C–H functionalization reactions of substrates with a bidentate 8-aminoquinoline directing group (Scheme 1C). Besides one theoretical investigation of the mechanism of this type of reaction, little information is available on the elementary steps for substrate activation and product formation. Inspired by this observation and given our interest in bifunctional substrate activation using reactive ligands as well as applications of redox-active ligands, we set out to study the chemistry of model Ni-alkyl complexes bearing a pincer ligand featuring a flanking aryl fragment.
for the corresponding Ni–CH₃ complex and the resulting Niᴵᴵᴵ species, relevant in the context of C₆₋₇–C₆₇ reductive elimination, may potentially be detectable. Previous reports show that CF₃ ligands can stabilize the Niᴵᴵᴵ oxidation state in [Niᴵᴵᴵ(tBu₃tpy)(CF₃)₂]⁺ (tBu₃tpy = 4,4',4''-tris(tert-butyl)-2,2':6,2''-terpyridine). Reductive elimination from Niᴵᴵᴵ would result in formation of a formally Niᴵ species, which are also considered of relevance, e.g., for cross-coupling catalysis and for metallo-radical-induced reactivity.

One-electron reduction of the Niᴵᴵ–alkyl complexes might lead to the formation of Niᴵ species [Niᴵ(alkyl)(κ³-P,N,C-PONC)]⁻ or alternatively to Niᴵ complexes with a radical anionic ligand [Niᴵ(alkyl)(κ³-P,N,C-PONC⁻)]⁻ and the nature of the alkyl ligand might be decisive for the specific character of these reduced species. This is in analogy to tpy complexes with [Ni(tpy)(R)]⁺ (R = alkyl or aryl) that show clear evidence for Niᴵ coordinated to reduced tpy⁻, while [Ni(tpy)(X)]⁺ (X = I, Br, Cl) species are best described as Niᴵ species.

We used a combination of cyclic voltammetry, UV/Vis spectrophotometry, and chemical oxidants or reductants in combination with EPR spectroscopy and supported by DFT calculations to study the redox chemistry of these two complexes in detail on which we will report herein. These findings may be relevant not only for the modelling of carbon–carbon bond forming reactions but also in the application of redox-active ligands in catalysis, which is an emerging field of research.

Results and Discussion

Complexes 2CH₃ and 2CF₃ are both synthesized from the previously reported complex 1. The Me group in complex 2CH₃
can be easily installed via simple transmetalation using MeLi and 1 in toluene (Scheme 3), which results in an immediate color change from yellow to red. The desired product shows a small downfield shift in $^{31}$P NMR compared to complex 1 ($\delta = 194$ ppm vs. 187 ppm) and the corresponding $^1$H NMR spectrum contains an upfield signal at $\delta = -0.06$ ppm ($J_{PH} = 9.1$ Hz) that is assigned to the Ni-bound CH$_3$ ligand. Crystals suitable for X-ray analysis were grown by slow evaporation of an Et$_2$O solution (Figure 1) and the molecular structure shows Ni–CH$_3$ 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 (more details in the Experimental Section). Complex 2CF$_3$ is prepared by reacting 1 with CsF and TMS–CF$_3$, Ruppert's reagent, in THF. Complex 2CF$_3$ shows a quartet in $^{31}$P NMR at $\delta = 195$ ppm with a coupling constant $J_{PF}$ of 26 Hz and a doublet at $\delta = 11$ ppm with the same coupling constant is found in $^{19}$F NMR spectroscopy. In the $^{13}$C NMR spectrum a signal is evident for the CF$_3$ ligand at $\delta = 144$ ppm with a coupling constant $J_{PC}$ of 18 Hz and a large coupling constant $J_{CF}$ of 357 Hz, which is similar to other reported Ni–CF$_3$ complexes. Single crystals of 2CF$_3$ were obtained by slow solvent evaporation from a solution of 2CF$_3$ in diethyl ether. The molecular structure is similar to complex 2CH$_3$ although the Ni–CF$_3$ bond is slightly contracted in comparison to the Ni–CH$_3$ bond [1.878(3) Å; $\Delta d$ vs. Ni–CH$_3$ of at least 0.055 Å]. This phenomenon is common and can be explained by the stronger binding of the CF$_3$ group to Ni. Another reported difference between Ni–CH$_3$ and Ni–CF$_3$ complexes is the stabilization of the HOMO and the LUMO by the CF$_3$ ligand.

To analyze whether this also holds for complexes 2CH$_3$ and 2CF$_3$, we resorted to DFT calculations. After structure optimization, the energy levels of the frontier molecular orbitals were determined. Table 1 shows the comparison of the energy levels of the HOMO and LUMO of 2CH$_3$ and 2CF$_3$. The calculated HOMO of complex 2CF$_3$ is stabilized by 0.5 eV relative to 2CH$_3$, which will probably result in a higher oxidation potential for 2CF$_3$. On the other hand, also the LUMO of 2CF$_3$ is stabilized by 0.3 eV, which should translate to reduction at less negative potential.

![Scheme 3. Synthesis of Ni–alkyl complexes 2CH$_3$ and 2CF$_3$ from precursor 1.](image)

![Figure 1. ORTEP plots (50 % probability) for 2CH$_3$ (left) and 2CF$_3$ (right) (See Experimental Section for details). Selected bond lengths [Å] and angles [°] for 2CH$_3$: Ni1–C12 1.933(4); Ni1–C1 1.925(3); Ni1–N1 1.902(3); Ni1–P1 2.151(1); C1–Ni1–N1 84.0(1); C1–Ni1–C12 93.4(2); C12–Ni1–P1 100.4(1); C1–Ni1–P1 166.7(1); For 2CF$_3$: 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 166.7(1).](image)

<table>
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<th>Complex</th>
<th>HOMO [eV]</th>
<th>LUMO [eV]</th>
<th>Gap [eV]</th>
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<td>2CF$_3$</td>
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<td>-2.747</td>
<td>1.932</td>
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</table>

Table 1. DFT calculated energy levels of the frontier orbitals of complexes 2CH$_3$ and 2CF$_3$.

[a] Structures optimized with Turbomole (BP86, def2-TZVP, disp3).
The stabilizing effect of the CF₃ ligand was also apparent by mass spectrometry. For complex 2CF₃, the molecular ion peak was observed using Electron Spray Ionization (ESI) at m/z 442.1077, while only fragmented ion peaks were found for complex 2CH₃. Field Desorption (FD), showed a main fragmentation at m/z 345.2762 for 2CH₃, which could correspond to a methylated ligand structure with a phosphine oxide (calculated mass of 345.1858). This result indicates that complex 2CH₃, in contrast to complex 2CF₃, is relatively unstable toward reductive elimination upon ionization.

Oxidation of NiIII Species 2CH₃ and 2CF₃

The electrochemistry of both alkyl complexes was probed with cyclic voltammetry. For complex 2CH₃, the cyclic voltammogram in PrCN revealed irreversible oxidation events at –0.08 V and +0.77 V, regardless of the temperature (room temp. or –55 °C) or scan rate (Figure 2, left). For 2CF₃ a first irreversible oxidation wave was observed at +0.51 V, with an equally irreversible follow-up event at +0.88 V. Thus, the alkyl ligand has a strong impact on the oxidation processes, in line with a metal-centered (NiII/NiIII) oxidation. These redox events, postulated to form NiIII intermediate species, are likely coupled to follow-up C–C bond-forming reductive elimination of the alkyl fragment and the phenyl ring of the PNC ligand, generating a NiI complex A with the ligand only coordinating via the P and the N donors, as well as solvent molecules to fulfill the coordination sphere requirements around Ni. Chemical oxidation of 2CH₃ at room temp. in a mixture of PrCN/MeCN (3:1) using the mild oxidant [acyethylferrocenium]BF₄ ([(Fe(η⁵-C₅H₅)(C≡CH)(O)Me(η⁵-C₅H₅)])BF₄) led to a color change from dark blue to orange. EPR spectroscopy of the frozen sample at 30 K revealed a well-defined rhombic spectrum (Figure 2, middle) with well-resolved hyperfine interactions related to a single phosphorus atom. This spectrum could be simulated with the g- and A-tensor components shown in Table 2. Reductive elimination of the one-electron oxidized species [NiIII(Me)(κ³-PN-C-PONC)]⁺ would lead to a C₃C₄ bond in a [Ni⁺(κ²-PN-PONC-Me)]⁺ species with a pending tolyl group at the phosphino–pyridine ligand. DFT calculations of the EPR parameters for the optimized geometry of solvated NiII complex A, [Ni⁺(NCMe)₂(κ²-PN-PONC-Me)]⁺ (structure optimized with Turbomole) showed good agreement with the experimentally obtained EPR data, using either ORCA or ADF (Figure 2, right). The calculated EPR parameters of the putative optimized NiII species B, [Ni(II–PNC)(NCMe)(κ²-PN-C-PONC)]⁺ were very different, with a nearly axial g tensor and much smaller phosphorus hyperfine interactions (Table 2).

These results are in line with anodic UV/Vis spectrophotometry of complex 2CH₃ (Figure 3), which clearly shows the bleaching of the long-wavelength band at 454 nm, presumably corresponding to a metal-to-ligand charge transfer (MLCT) and the blue shift of a π→π* band at 315 nm to 292 nm indicating both the reduction of the metal. Furthermore, 2CH₃ and 2CF₃ were anodically oxidized in the presence of the spin trap PBN (N-tert-buty1-α-phenylnitrone) in the EPR cavity but no signals of PBN adducts of either alkyl fragment, indicative for the formation of -CH₃ or -CF₃ radicals, were observed. Such signals have been observed upon oxidation of the complexes [Ni(BOXAM)(alkyl)] (BOXAM = bis((4-isopropyl-4,5-dihydrooxaz-...
ol-2-yl)(phenyl)amine) bearing either CH₃ or CF₃ as alkyl ligand, which suggest formation of a species containing Ni⁺ and the oxidized BOXAM ligand (aminyl radical).[9]

Use of one equiv. AgBF₄ as chemical oxidant in MeCN led to a precipitate and still ±50 % starting complex 2CH₃, judging from UV/Vis spectroscopy, whereas with two equiv. AgBF₄ a well-defined new signal at δ = 2.26 ppm in the ¹H NMR spectrum was detected, assigned to the Ph–CH₃ group (Figure 4, left). Furthermore, the aromatic region showed typical signals for a freely rotating phenyl ring, rather than a cyclometalated analog, that integrate for four protons. The ³¹P NMR spectrum showed two slightly broadened overlapping doublets (Figure 4, right) at δ = 139.1 ppm, ¹JAg-P = 707 Hz (¹⁰⁷Ag isotope) and ¹JAg-P = 618 Hz (¹⁰⁹Ag isotope), plus an even more broadened side product with similar features. These combined spectroscopic data correspond well with those of related complexes already reported by Klausmeyer.[29] The main product is thus attributed to a dimeric Ag complex with the phosphino–pyridine ligand acting as a bridging dinucleating framework in [Ag₂(κ²-P₂N₆PNC-Me)₂] (B). This species would be formed upon transfer of the ligand from Ni⁺ to Ag⁺. The observed NMR broadening likely corresponds to fast reversible dissociation of the phosphine donors.[29] Using high resolution cold-spray ionization (CSI) mass spectrometry a molecular ion peak was detected at m/z = 477.1248, supporting the formation of this dinuclear silver species B.

Transmetalation of the ligand from Ni⁺ to Ag⁺ upon C–C reductive elimination was also supported by the rudimentary detection of crystalline [Ni⁺(NCMe)₆]BF₄ (by X-ray diffraction) that separated from the reaction mixture, which may suggest a disproportionation reaction of unstable [Ni⁺(NCMe)₆]BF₄ into a Ni⁰ species and the aforementioned characterized Ni⁺ species. The oxidation of 2CF₃ with (thianthrenium)BF₄ in [D₃]MeCN in the presence of AgBF₄ led to similar ³¹P NMR features, whilst the ¹⁹F NMR spectrum contained a signal at δ = −57 ppm, indicative of the formation of a CPh–CCF₃ fragment via reductive elimination.[30] CSI-HRMS also supported formation of the dinuclear Ag complex after transmetalation, with a molecular ion peak at m/z 531.0953. (Scheme 4).

Reduction of Ni⁺ Species 2CH₃ and 2CF₃

To probe any possible reduction events with both alkyl species, we again initially resorted to cyclic voltammetry. The cyclic voltammograms of 2CH₃ and 2CF₃ show a reversible reduction wave at E₁/₂ = −2.60 V and −2.36 V, respectively (Figure 5). The
observed difference in reduction potentials of $2\text{CH}_3$ and $2\text{CF}_3$ is in agreement with the DFT calculations, which predicted that the reduction of $2\text{CF}_3$ 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 $2\text{CF}_3$ has a small shoulder which is most likely a small impurity.

UV/Vis spectrophotometric studies were performed in THF, in which both complexes show similar behavior. The reduction event of $2\text{CH}_3$ occurs at very negative potential, resulting in interference of solvent reduction. This problem is not observed for $2\text{CF}_3$ and upon spectrophotometric reduction, three new broad and partially structured bands appear in the NIR and visible region at $\lambda = 1090, 661$ and 430 nm, while the initial bands at 393 and 343 nm either shift to higher energy or disappear (Figure 6). The very intense band at $\lambda = 245$ nm is reduced in intensity to about 50%. These features are reminiscent of the ligand-centered reduction of bipyridine complexes, e.g., quite similar absorptions were recently reported for the radical anionic Ni$^{III}$ complex $[\text{Ni}^{III}\text{Br}(\text{Phbpy})]^{--}$ (HPhbpy = 6-phenyl-2,2'-bipyridine). The combined data clearly indicate a reduction centered at the phenylpyridine core of the ligand of $2\text{CF}_3$ to furnish complex $[3\text{CF}_3]^{--}$, which is best described as Ni$^{II}$ bound to a radical anionic ligand $[\text{Ni}^{II}\text{CF}_3(\kappa_3-\text{P}^0\text{NC})]^{--}$ rather than a Ni$I$ complex. To find further evidence to support that the reduction is ligand centered, complexes $2\text{CH}_3$ and $2\text{CF}_3$ were treated with KC$_8$ in THF, resulting in a slight darkening of the solutions (Scheme 5).

The EPR spectrum of compound $[3\text{CH}_3]^{--}$ measured in isotropic solution is characteristic for a ligand-radical complex and reveals a set of well-resolved hyperfine couplings (Figure 7). A
Figure 6. UV/Vis spectroelectrochemical reduction of complex $2\text{CF}_3$ in THF/$(n\text{Bu})_4\text{PF}_6$ cathodic scan from 0 V to –2.2 V (referenced to Ag/Ag+).

Scheme 5. Proposed anionic ligand radical species $[3\text{CH}_3]^{·–}$ and $[3\text{CF}_3]^{·–}$ from reaction of $2\text{CH}_3$ and $2\text{CF}_3$ with KC₈.

A satisfactory simulation was obtained with the parameters shown in Table 3 and DFT computed EPR parameters are in agreement with the experimental data. A very similar EPR spectrum (see Supporting Information) was obtained through cathodic reduction of $2\text{CH}_3$ in $(n\text{Bu})_4\text{PF}_6$/THF in the EPR cavity (EPR spectroelectrochemistry).

For complex $[3\text{CF}_3]^{·–}$ a similar signal was observed in EPR, although the hyperfine splitting was less resolved (see Supporting Information). The combined data strongly indicate the formation of a PNC ligand radical anion formed in the coordination sphere of NiII, with the unpaired electron spread out across most of the phenyl–pyridine framework, as deduced from the DFT computed electronic structure of $[3\text{CH}_3]^{·–}$ – the SOMO and spin density plots of $[3\text{CH}_3]^{·–}$ are shown in Figure 6 (middle and right, respectively).

Thus, both reduced complexes $[3\text{CH}_3]^{·–}$ and $[3\text{CF}_3]^{·–}$ are best described as NiII complexes containing a radical anionic PONC ligand [NiII(alkyl)(κ₃-P,N,C-PONC)·–] in analogy to the previously

Table 3. Experimental and DFT calculated EPR parameters of $[3\text{CH}_3]^{·–}$.

<table>
<thead>
<tr>
<th></th>
<th>Exp.[a]</th>
<th>DFT (ORCA)[b]</th>
<th>DFT (ADF)[c]</th>
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<td>3.8</td>
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[a] Values obtained by spectral simulation. [b] ORCA, B3LYP, def2-TZVP. [c] ADF, B3LYP, TZ2P.

Figure 7. Left: Experimental and simulated X-band EPR spectra of NiII–ligand radical complex $[3\text{CH}_3]^{·–}$ measured in isotropic solution (THF) at room temp. Experimental conditions: Temperature = 298 K, microwave power 2.0 mW, field amplitude = 1 Gauss, microwave frequency = 9.390764 GHz. The simulated spectrum was obtained with the parameters shown in Table 3. (Middle) SOMO of complex $[3\text{CH}_3]^{·–}$ (Turbomole, BP86, def2-TZVP). (Right) Spin density plot of complex $[3\text{CH}_3]^{·–}$ (Turbomole, BP86, def2-TZVP).
studied radical complex species [Ni(R)(terpy)]+ (terpy = 2,2′6,2″-terpyridine) with R = alkyl or aryl. [26] In the context of our current interest to bridge the fields of redox-active and re-active ligand design, these findings of ligand-centered one-electron reduction of the cyclometalated PNC platform, which was already shown to be chemically responsive in our previous work, [20–22] may prove a step in this direction.

Conclusions

The four-coordinate nickel–alkyl complexes [Ni(alkyl)(κ-3-PN,C-PONC)] with alkyl = CH3 (2CH3) or CF3 (2CF3), stabilized by a cyclometalated PNC pincer ligand have been synthesized and fully characterized. Both complexes show irreversible oxidation events in cyclic voltammetry that are likely coupled to C–C bond-forming reductive elimination. Bulk oxidation experiments yielded strong evidence for a NiI complex from EPR spectroscopy and DFT calculations on the assumed species [Ni(κ3-PN,C-PONC)(Me)(MeCN)]+ containing a pendant 2-tolyl group from reductive Calkyl–CPh bond formation, gave EPR parameters fully in line with the experimental data. Moreover, these complexes show reversible reduction, as judged from a combined experimental and computational study including spectroelectrochemistry, EPR spectroscopy and DFT calculations. Both spectroelectrochemistry and EPR point out that it is possible to reduce the phenylpyridine core of the ligand to produce a ligand-centered radical. In this way, the cyclometalated PNC platform which was already shown to be chemically responsive, can be included into the family of non-innocent ligands. [32]

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, n-pentane, n-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) were acquired on a Bruker DRX 500 MHz spectrometer using standard Bruker pulse sequences and analyzed with TopSpin 2.1 software. All spectra were run on CD3CN with TMS as an internal standard. Mass spectra were recorded on a Bruker microTOF-QII mass spectrometer using electrospray ionization (ESI) or chemical ionization. FTIR spectra were recorded on a Bruker Vertex 70 FTIR spectrometer using KBr pellets. UV/Vis spectra were obtained using a Cary 5000 spectrophotometer. HRMS (ESI) analyses were performed on a Bruker Daltonics microTOF-QII mass spectrometer using electrospray ionization (ESI) or chemical ionization. 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, n-pentane, n-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) were acquired on a Bruker DRX 500 MHz spectrometer using standard Bruker pulse sequences and analyzed with TopSpin 2.1 software. All spectra were run on CD3CN with TMS as an internal standard. Mass spectra were recorded on a Bruker microTOF-QII mass spectrometer using electrospray ionization (ESI) or chemical ionization. FTIR spectra were recorded on a Bruker Vertex 70 FTIR spectrometer using KBr pellets. UV/Vis spectra were obtained using a Cary 5000 spectrophotometer. HRMS (ESI) analyses were performed on a Bruker Daltonics microTOF-QII mass spectrometer using electrospray ionization (ESI) or chemical ionization.

[Ni(CF3)(κ-3-PN,C-PONC)] (2CF3): 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-CF3 (2.0 mL in THF) (0.27 mL, 0.53 mmol) was added dropwise and the reaction was stirred overnight. Subsequently, more TMS-CF3 (0.13 mL, 0.27 mmol) was added and the reaction was stirred for an additional four hours. THF was evaporated and the product was extracted with n-pentane. After filtration, the solvent was evaporated to yield 2CF3 as a yellow solid (0.078 g, quantitative). Crystals suitable for X-ray analysis were grown by slow evaporation of an Et2O solution. 1H NMR (300 MHz, CD3CN, ppm): δ = 7.94 (s, 1 H), 7.78 (d, JPH = 8.0 Hz, 1 H, Py-CH), 7.39 (d, JPC = 16.5 Hz, 2 H, CH3), 7.23 (d, JPH = 5.7 Hz, 1 H, Py-CH), 7.19 (s, 1 H, Ph-CH3), 7.06 (d, JPH = 5.8 Hz, 1 H, Py-CH), 6.80 (d, JPH = 8.2 Hz, 1 H, Py-CH), 1.41 [d, JPH = 13.6 Hz, 18 H, (CH3)3CP], –0.06 [d, JPH = 9.1 Hz, 3 H, Ni-CH2]. 31P NMR (121 MHz, CD3CN, ppm): δ = 194.28. 13C NMR (75 MHz, CD3CN, ppm): δ = 184.34 (d, JPC = 6.5 Hz, 2 H, Ph-C), 153.05 (s, 1 H, Py-CH), 150.49 (s, 1 H, Py-CH), 142.70 (s, 1 H, Py-CH), 138.41 (s, 1 H, Py-CH), 136.92 (s, 1 H, Py-CH), 134.68 (s, 1 H, Py-CH), 133.96 (s, 1 H, Py-CH), 130.26 (s, 1 H, Py-CH), 129.08 (s, 1 H, Py-CH), 127.96 (s, 1 H, Py-CH), 126.99 (s, 1 H, Py-CH), 125.91 (s, 1 H, Ph-CH), 118.96 (s, 1 H, Py-CH), 117.33 (s, 1 H, Py-CH), 115.43 (s, 1 H, Py-CH), 109.77 (s, 1 H, Py-CH).
Oxidation of $2\text{CF}_3$: A solution of [thianthrenium][BF$_4$]$_2$ (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. Oxidation at low temperature: sample was prepared outside the glovebox at –78 °C and precooled solutions and EPR tube. The sample was directly frozen in liquid N$_2$.

Oxidation of $2\text{CF}_3$ with [thianthrenium][BF$_4$] in the presence of AgBF$_4$: To a Schlenk containing complex $2\text{CF}_3$ (10 mg, 0.023 mmol), [thianthrenium][BF$_4$]$_2$ (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 thianthren, the product was only characterized in situ.

$\delta$H NMR (300 MHz, [D$_3$]MeCN, ppm): δ 8.00–7.67 (m, 4 H, Py-CH and 3 Ph-CH), 7.55 (thianthrene and 1 Py-CH), 7.33 (m, thianthrene), 7.25 (d, $J = 7.38$ Hz, Py-CH), 7.12 (d, $J = 8.30$ Hz, Py-CH), 1.24 (d, $J = 15.5$ Hz, CH$_2$(CF)$_3$), 3.1P NMR (121 MHz, [D$_3$]MeCN, ppm): δ 138.35 (m). $\delta$F NMR (282 MHz, [D$_3$]MeCN, ppm): δ $-57.25$ (s, Ph-CF$_3$), $-151.76$ (s, BF$_4$). HRMS (CSI): $C_23H_{28}AgF_3N_2O.P$: 531.0942 [M]+; found: 531.0953.

Reduction of $2\text{CH}_3$: K$_2$C$_3$H$_5$N$_2$O$_2$ (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 min at room temp. The reaction mixture was filtered and 0.2 mL was transferred to a capillary inside an EPR tube.

Reduction of $2\text{CF}_3$: K$_2$C$_3$H$_5$N$_2$O$_2$ (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 min at room temp. The reaction mixture was filtered and 0.2 mL was transferred to a capillary inside an EPR tube.

Electrochemistry: All cyclic voltammograms are measured in propionitrile with N(NBu$_4$)PF$_6$ (0.1 M) as the supporting electrolyte. Concentration of the analyte: 6 mM. Working electrode: glassy carbon. Counter electrode: Pt coil. Reference electrode: Ag coil. Scan rate: 100 mV s$^{-1}$. All redox potentials are referenced to ferrocene/ferrocinium (Fc/Fc$^+$).

X-ray Crystallography Studies

X-ray intensities were measured on a Bruker D8 Quest Eco diffractionometer equipped with a Triumph monochromator ($\lambda = 0.71073$ A) and a CMOS Photon 50 detector at a temperature of 150(2) K. Intensity data were integrated with the Bruker APEX2 software.[52] Absorption correction and scaling was performed with SADABS.[53] The structures were solved using intrinsic phasing with the program SHELXTL.[52] Least-squares refinement was performed with SHELX-2013[54] against $F^2$ of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were placed at calculated positions using the instructions AFFIX 13, AFFIX 43 or AFFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times $U_{eq}$ of the attached C atoms.

CCDC 1821417 (for $2\text{CF}_3$) and 1821418 (for $2\text{CH}_3$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

For $2\text{CH}_3$: C$_{20}$H$_{25}$NiOP, $F_w = 388.11$, $T = 150$ K, orange plate, 0.197 × 0.221 × 0.431 mm$^3$, monoclinic, $C2/c$ (no. 15), $a = 43.970(3)$ Å, $b = 14.3860(10)$ Å, $c = 24.9872(16)$ Å, $\beta = 94.7917(9)^\circ$, $V = 15750.5$ Å$^3$, $Z = 34$, $D_x = 1.395$ g cm$^{-3}$, $\mu = 1.140$ mm$^{-1}$. 221290 Reflections were measured up to a resolution of (sin $\theta/\lambda_{\text{max}}$) = 0.993 Å$^{-1}$. 14101 Reflections were unique ($R_{\text{int}} = 0.1050$), of which 9722 were observed ($l > 2\sigma(l)$). 893 Parameters were refined with no restraints. $R_{1}/wR_{2}$ ($l > 2\sigma(l)$): 0.0430/0.1084. $R_{1}/wR_{2}$ [all refl.]: 0.0385/0.1331. $S = 0.848$. Residual electron density found between $-0.36$ and 0.44 eÅ$^{-3}$.

For $2\text{CF}_3$: C$_{20}$H$_{25}$F$_3$NiOP, $F_w = 442.08$, $T = 150$ K, yellow plate, 0.106 × 0.162 × 0.335 mm$^3$, monoclinic, $P2_1/c$ (no. 19), $a = 8.1987(10)$ Å, $b = 10.5103(13)$ Å, $c = 23.341(6)$ Å, $V = 2011.31$ Å$^3$, $Z = 4$, $D_x = 1.460$ g cm$^{-3}$, $\mu = 1.080$ mm$^{-1}$. 40175 Reflections were measured up to a resolution of (sin $\theta/\lambda_{\text{max}}$) = 0.989 Å$^{-1}$. 5061 Reflections were unique ($R_{\text{int}} = 0.0825$), of which 3840 were observed ($l > 2\sigma(l)$). 250 parameters were refined with no restraints. $R_{1}/wR_{2}$ ($l > 2\sigma(l)$): 0.0428/0.0617. $R_{1}/wR_{2}$ [all refl.]: 0.0824/0.0690. $S = 1.028$. Residual electron density found between $-0.68$ and 0.74 eÅ$^{-3}$.

Complex $2\text{CH}_3$: Selected bond lengths [Å] and angles [°] for the other three independent molecules found in the unit cell: Ni2–C12–C12 1.943(4); Ni2–C12–I 1.933(4); Ni2–C12–I 1.910(3); Ni2–P1B 2.161(1); C12–Ni2–C12 83.9(2); C12–Ni2–C12 92.4(2); C12–Ni2–C12 100.6(1); P1B–Ni2–C12 83.1(1); C12–Ni2–P1B 166.9(1). For Ni3: Ni3–C12–C12 1.957(4); Ni3–C12–I 1.939(4); Ni3–C12–I 1.916(3); Ni3–P1B 2.173(1); C12–Ni3–N1C 83.6(2); C12–Ni3–C12 93.2(2); C12–Ni3–P1C 100.2(1); P1C–Ni3–N1C 83.1(1); C12–Ni3–P1C 166.1(1). For Ni4: Ni4–C12–C12 1.958(4); Ni4–C12–I 1.939(4); Ni4–C12–I 1.913(4); Ni4–P1B 2.162(1); C10–Ni4–N1D 84.0(1); C10–C12–C12 93.4(2); C10–Ni4–P1D 99.8(1); P1D–Ni4–N1D 82.8(9); C10–Ni4–P1D 166.9(1).

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