Nickel–Alkyl Complexes with a Reactive PNC-Pincer Ligand


Abstract: Based on previous work related to the design and application of rigid tridentate phosphine–pyridine–phenyl coordination offered by a PNC-pincer ligand upon cyclometalation to nickel, the synthesis, spectroscopic and solid state characterization and redox-reactivity of two NiII(PNC) complexes featuring either a methyl (2CH₃) or CF₃ co-ligand (2CF₃) are described. One-electron oxidation is proposed to furnish C–C reductive elimination, as deduced from a combined chemical, electrochemical, spectroscopic and computational study. One-electron reduction results in a ligand-centered radical anion, as supported by electrochemistry, UV spectrophotometry, EPR spectroscopy, and DFT calculations. This further attenuates the breadth of chemical reactivity offered by such PNC-pincer ligands.

Introduction

Nickel–alkyl species have become relevant for a wide variety of C–C bond-forming reactions, including Negishi, Suzuki–Miyaura, Stille, Kumada and Hiyama couplings.[1,2] The trifluoromethylation of arenes is industrially interesting because of the intriguing properties of fluoroorganic materials.[3] 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.[4] It was proposed that Ni could be an active catalyst for this transformation,[5,6] and the precise understanding of Ni–CF₃ bonding and reactivity of these complexes have been subject to several studies, usually in comparison to Ni–CH₃ bonding.[7–12] 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.[13] 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).[14] 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-aminquinoline directing group (Scheme 1C).[15,16] Besides one theoretical investigation of the mechanism of this type of reaction,[17] 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[18] as well as applications of redox-active ligands,[19] we set out to study the chemistry of model Ni-alkyl complexes bearing a pincer ligand featuring a flanking aryl fragment.

We previously reported a new family of PNC pincer ligands L₃H (X = CH₂ or O; Scheme 2) that are susceptible to facile reversible cyclometalation at the flanking phenyl substituent in the case of RhI precursor complexes.[20] We also reported selective reprotonation of the Rh–CPh bond to afford the crystallographically characterized complex [RhCl(CO)(κ3-PN-HLCH₂)] with a reprotonated phenyl substituent that is still in the first coordination sphere of RhI. This platform also enabled Rh-catalyzed formic acid dehydrogenation using the metal–ligand bifunctional strategy.[21] Satisfyingly, the same flexible coordination chemistry was available with nickel, including base-mediated cyclometalation directly from a NiII precursor to provide a [NiIIBr(κ3-PN,C₂-PONC)] complex and subsequent reprotonation of the nickel–C₈H₈ bond.[22]

Beyond the reversible nature of the nickel–carbon bond, the cyclometalated nickel species also offers substitution chemistry at the Ni–Br fragment. We therefore decided to synthesize square planar [NiII(alkyl)(κ3-PN,C₂-PONC)] complexes that contain either a CH₃ or CF₃ as alkyl ligand. Oxidation of such a Ni–CF₃ complex is expected to occur at more positive potential than
Scheme 1. (A) a recently published model for aryl–alkyl coupling (adapted from ref.[14]). (B) the model system for a constrained phenyl ligand used in this work. (C) C–H functionalization using the directing group approach (adapted from ref.[15]).

Scheme 2. Reversible cyclometalation reactivity of novel PXNC-pincer platforms LXH with RhI and NiII.

for the corresponding Ni–CH3 complex and the resulting NiIII species, relevant in the context of CAr–Calkyl reductive elimination, may potentially be detectable.[23] 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).[24] 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.[25]

One-electron reduction of the NiIII–alkyl complexes might lead to the formation of NiI species [NiI(alkyl)(κ3-P,N,C-PONC)]– or alternatively to NiII complexes with a radical anionic ligand [NiII(alkyl)(κ3-PN,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 NiII coordinated to reduced tpy·–, while [Ni(tpy)(X)]+ (X = I, Br, Cl) species are best described as NiI species.[26]

We used a combination of cyclic voltammetry, UV/Vis spectroelectrochemistry, 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.[22] 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$^{[27]}$ 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$^{[8,28]}$. 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$^{[4,11,12]}$. 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.

Table 1. DFT$^{[a]}$ calculated energy levels of the frontier orbitals of complexes 2CH$_3$ and 2CF$_3$.

<table>
<thead>
<tr>
<th>Complex</th>
<th>HOMO [eV]</th>
<th>LUMO [eV]</th>
<th>Gap [eV]</th>
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<tr>
<td>2CH$_3$</td>
<td>-4.215</td>
<td>-2.432</td>
<td>1.783</td>
</tr>
<tr>
<td>2CF$_3$</td>
<td>-4.679</td>
<td>-2.747</td>
<td>1.932</td>
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$^{[a]}$ Structures optimized with Turbomole (BP86, def2-TZVP, disp3).

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 99.7(1); P1–Ni1–N1 83.0(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); N1–Ni1–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).

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 fragment 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 towards reductive elimination upon ionization.

Oxidation of NiII 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 a single phosphorus atom. This spectrum could be simulated with the fine interactions related to a single phosphorus atom. This spectrum could be simulated with the fine interactions related to a single phosphorus atom.

Table 2. The experimental spectrum was recorded at 30 K in frozen PrCN/MeCN 3:1. Microwave frequency = 9.363973 GHz, modulation amplitude=4G auss, simulated X-band EPR spectra of proposedly complex 442.1077, while only fragmented ion peaks were found for complex 345.1858)

<table>
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<th>Experimental[a]</th>
<th>(ORCA)[b]</th>
<th>(ADF)[c]</th>
<th>DFT (ORCA)[d]</th>
<th>(ADF)[d]</th>
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<td>NiI B</td>
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<td>2.195</td>
<td>2.204</td>
</tr>
<tr>
<td>A'</td>
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<td>ρP(b)[e]</td>
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<td>0.83</td>
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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-tet-butyl-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 NiII 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-PN-P³NC-Me)₂] (B). This species would be formed upon transfer of the ligand from NiI to AgI. 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 NiI to AgI upon C–C reductive elimination was also supported by the rudimentary detection of crystalline [NiI(NCMe)₆]BF₄ by X-ray diffraction) that separated from the reaction mixture, which may suggest a disproportionation reaction of unstable [NiI(NCMe)₆]BF₄ into a Ni⁰ species and the aforementioned characterized NiII 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 NiII 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

Figure 3. UV/Vis spectroelectrochemical oxidation of a solution of complex 2CH₃ in THF/(nBu)₄PF₆; anodic scan from 0 V to +1.2 V (referenced to Ag/Ag⁺).

Figure 4. Left: ¹H NMR spectrum in [D₃]MeCN from the reaction of complex 2CH₃ with two equivalents of AgBF₄. Right: corresponding ³¹P NMR spectrum.
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 spectroelectrochemistry was 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 spectroelectrochemical reduction, three new broad and partially structured band systems in the NIR and visible region appear with maxima at $\lambda = 1090$, 661 and 430 nm, and one intense new band in the UV region at $\lambda = 324$ 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$^{II}$ complex $[\text{Ni}^{II}\text{Br}(\text{HPhbpy})^{−}]$ (HPhbpy = 6-phenyl-2,2’-bipyridine).[31] 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 $[\text{Ni}^{II}(\text{CF}_3)^{(κ^2-P-\text{PONC})}^{−}]$ 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
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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⁺).


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 $[3\text{CF}_3]^- – [3\text{CH}_3]^- – [3\text{CF}_3\text{CF}_3]^- – [3\text{CF}_3\text{CF}_3]^-$ 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 $[3\text{CH}_3]^- – [3\text{CF}_3]^- – [3\text{CH}_3\text{CF}_3]^- – [3\text{CF}_3\text{CF}_3]^-$. The SOMO and spin density plots of $[3\text{CH}_3]^- – [3\text{CF}_3]^- – [3\text{CH}_3\text{CF}_3]^- – [3\text{CF}_3\text{CF}_3]^-$ are shown in Figure 6 (middle and right, respectively).

Thus, both reduced complexes $[3\text{CH}_3]^- – [3\text{CF}_3]^- – [3\text{CH}_3\text{CF}_3]^- – [3\text{CF}_3\text{CF}_3]^-$ 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>
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<th></th>
<th>Exp.[a]</th>
<th>DFT (ORCA)[b]</th>
<th>DFT (ADF)[c]</th>
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[a] Values obtained by spectral simulation. [b] ORCA, B3LYP, def2-TZVP. [c] ADF, B3LYP, TZ2P.

studied radical complex species [Ni⁴(R(terpy′))] (terpy = 2,2′:6′:2″-terpyridine) with R = alkyl or aryl.⁴ 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 provide a step in this direction.

Conclusions

The four-coordinate nickel–alkyl complexes [Ni[alkyl](κ²-PRC-P(POC))] with alkyl = CH₃ (2CH₃) or CF₃ (2CF₃), stabilized by a cyclometalated PNC pincer ligand have been synthetized 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 Ni¹ complex from EPR spectroscopy and DFT calculations on the assumed species [Ni(κ²-PNC-P(POC)-(Me)2MeCN)]⁺ 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, from sodium benzophenone ketyl, CH₂Cl₂ was distilled from CaH₂, by us.²² From reductive Calkyl–CPh bond formation, gave EPR parameters which was already shown to be chemically responsive, can 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

[Ni(CH₃)(κ²-PRC-P(POC))] (complex 2CH₃): Complex 1 (0.080 g, 0.18 mmol) was filtrated and precipitated with Celite and the solvent evaporated. The product was extracted with CH₂Cl₂, CHCl₃ or CF₃ (0.055 g, 80 %). Crystals suitable for X-ray analysis were grown by slow evaporation of an Et₂O solution.

Oxidation of 2CH₃: A solution of [acetylferrocenium]BF₄ (13 μmol, 4.1 mg) in a mixture of PrCN/MeCN = 3:1 (0.2 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 m 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.

[2CH₃]⁺: 1H NMR (300 MHz, [D₃]MeCN, ppm): δ = 7.91 (s, Ph-C), 17.91 (m, Py-CH₃), 7.38 (m, 2 H, Ph-CH₃), 7.32 (d, J = 7.3 Hz, 1 H, Py-CH₃), 7.30 (dd, J = 7.7 Hz, 0.8 Hz, 1 H, Py-CH₃), 7.20 (tt, J = 7.3, 1.7 Hz, 1 H, Ph-CH₃), 7.08 (td, J = 7.4, 1.4 Hz, 1 H, Ph-CH₃), 6.80 (d, J = 8.2 Hz, 1 H, Py-CH₃), 1.41 [d, J₁₉₆ = 13.6 Hz, 18 H, (CH₃)₃CP], –0.06 [d, J₂₉₆ = 9.1 Hz, 3 H, Ni-CH₃], 3¹P NMR (121 MHz, [D₃]MeCN, ppm): δ = 194.28. ¹⁳C NMR (75 MHz, [D₃]MeCN, ppm): δ = 165.74 (d, δ₁₉₆ = 92.2 Hz, Ni-C), 164.73 (d, J₁₉₆ = 4.5 Hz, Py-C), 164.01 (d, J₂₉₆ = 9.5 Hz, Py-C), 150.28 (s, Ph-C), 141.79 (s, Py-CH₃), 134.37 (s, Ph-CH₃), 130.21 (d, J₁₉₆ = 5.3 Hz, Ph-CH), 125.09 (s, Ph-CH), 123.09 (d, J₂₉₆ = 3.5 Hz, Ph-CH₃), 111.62 (s, Py-CH₃), 107.11 (d, J₁₉₆ = 4.0 Hz, Py-C), 39.16 (d, J₂₉₆ = 4.2 Hz, (CH₃)₃CP), 27.82 (d, J₂₉₆ = 6.8 Hz, (CH₃)₃CP), –10.92 (d, J₁₉₆ = 14.7 Hz, Ni-CH₃), UV/Vis (MeCN, nm): λ = 241 (ε = 1.7 × 10⁴ L mol⁻¹ cm⁻¹), 313 (ε = 7.8 × 10³ L mol⁻¹ cm⁻¹), 452 (ε = 1.3 × 10³ L mol⁻¹ cm⁻¹).

[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 m 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.

[2CH₃]⁺: 1H NMR (300 MHz, [D₃]MeCN, ppm): δ = 7.92 (t, J = 7.8 Hz, 1 H), 7.35 (m, 4 H), 7.22 (d, J = 5.2 Hz, 1 H), 7.03 (d, J = 8.0 Hz, 1 H), 2.26 (s, 3 H, Ph-CH₃), 1.25 (d, J = 15.4 Hz, 18 H, (CH₃)₃CP). ¹¹B NMR (121 MHz, [D₃]MeCN, ppm): δ = 139.12 (dd, J₁₉₆ = 707 Hz, J₂₉₆ = 67, J₂₉₆ = 618 Hz). ¹¹C NMR (75 MHz, [D₃]MeCN, ppm): δ = 162.30 (s, Ph-C), 158.20 (m, Py-C), 143.22 (s, Ph-CH₃), 140.83 (s, Ph-CH₃), 136.56 (s, Ph-C), 131.27 (s, Ph-CH₃), 130.36 (s, Ph-C), 129.64 (s, Ph-CH₃), 126.77 (s, Ph-CH₃), 112.31 (s, Ph-CH₃), 37.58–36.58 (m, (CH₃)₃CP), 27.16 (d, J₁₉₆ = 10.9 Hz, (CH₃)₃CP), 20.29 (s, Ph-CH₃). One of the Py-CH signals is obscured by the solvent residual signal. HRMS (CSI): m/z calcld. for C₂₂H₃₂AgN₂OP: 477.1225 [M⁺]; found: 477.1248.

Oxidation of 2CF₃: A solution of [thianthrenium]BF₄ (11 μmol, 3.2 mg) in a mixture of PrCN/MeCN = 3:1 (0.2 mL) was added to a solution of complex 2CF₃ (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 N₂ 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 N₂.

Reduction of 2CH₃: K₂C₂O₇ (13 μmol, 1.8 mg) was added to a solution of 2CH₃ (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 2CF₃: K₂C₂O₇ (11 μmol, 1.5 mg) was added to a solution of 2CF₃ (11 μmol, 5.0 mg) in THF (0.2 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)₄PF₆ (0.1 M) as the supporting electrolyte. Concentration of the analyte: 6 mM. Working electrode: glassy carbon. Counter electrode: Ag wire. Scan rate: 0.003 V s⁻¹. All redox potentials are referenced to ferrocene/ferrocenium (Fc/Fc⁺).

Spectroelectrochemistry: UV/Vis spectra were measured with an optical-transparent-thin-layer electrochemical OTTLE cell. The oxidation and reduction measurements were carried out in propionitrile, MeCN or THF, respectively, with N(nBu)₄PF₆ (0.2 M) as the supporting electrolyte. Working electrode: Pt. Counter electrode: Pt. Reference electrode: Ag wire. Scan rate: 0.003 V s⁻¹.

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) or a Bruker ELEXYS500E equipped with a Bruker variable-temperature unit ER 4131 VT (500 to 100 K). 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.

Computational Details and EPR Property Calculations: Geometry optimizations were carried out with the Turbomole program package[44–47] coupled to the QPS Baker optimizer[48] via the BOpt package,[49] at the n-DFT[50]/BP86[51,52] level. We used Grimmes D3 dispersion corrections (disp3)[53] and the def2-TZVP basis set[54,55] for all atoms, and a small grid (m4). EPR parameters[56,57] were subsequently calculated with the ADF[58–60] 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 were used, employing unrestricted SPINORBIT ZORA COLLINEAR calculations for the SOC corrected HFI-tensors and Zee-

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**X-ray Crystallography Studies**

X-ray intensities were measured on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator (λ = 0.71073 Å) 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 SHELXT[52]. Least-squares refinement was performed with SHELXL-2013[54] against F² of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were placed at calculated positions using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times Uiso of the attached C atoms. CCDC 1821417 (for 2CF₃) and 1821418 (for 2CH₃) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

**For 2CH₃**: C₂₀H₂₅F₃NNiOP, Fw = 388.11, T = 150 K, orange plate, 0.197 × 0.221 × 0.431 mm³, monoclinic, C2/c (no. 15), a = 34.970(3) Å, b = 14.4860(11) Å, c = 24.9872(16) Å, β = 94.791(7)°, V = 15750.5 Å³, Z = 34, Dₐ = 1.395 g cm⁻³, μ = 1.140 mm⁻¹. 221290 Reflections were measured up to a resolution of (sin θ/λ)max = 0.993 Å⁻¹. 14101 Reflections were unique (Rint = 0.1805), of which 9722 were observed (I > 2σ(I)). 893 Parameters were refined with no restraints. R1/wR2 (I > 2σ(I)): 0.0430/0.1084. R1/wR2 [all refl.]: 0.0835/0.1331. S = 0.848. Residual electron density found between –0.36 and 0.44 e Å⁻³.

**For 2CF₃**: C₂₀H₂₉NiOP, Fw = 442.08, T = 150 K, yellow plate, 0.106 × 0.162 × 0.335 mm³, monoclinic, P2₁/a (no. 19), a = 8.1987(10) Å, b = 10.5103(13) Å, c = 23.3417(11) Å, V = 2011.31 Å³, Z = 4, Dₐ = 1.460 g cm⁻³, μ = 1.080 mm⁻¹. 40175 Reflections were measured up to a resolution of (sin θ/λ)max = 0.988 Å⁻¹. 5061 Reflections were unique (Rint = 0.0825), of which 3840 were observed (I > 2σ(I)); 250 parameters were refined with no restraints. R1/wR2 (I > 2σ(I)): 0.0428/0.0617. R1/wR2 [all refl.]: 0.0824/0.0690. S = 1.028. Residual electron density found between –0.68 and 0.74 e Å⁻³.

**Complex 2CH₃**: Selected bond lengths [Å] and angles [°] for the other three independent molecules found in the unit cell: Ni2-N2-C12B 1.943(4); N2-C12B 1.933(4); Ni2-N18 1.910(3); Ni2-P1B 2.161(1); C1B-N2-C12B 83.9(2); C1B-N2-C12B 92.4(2); C1B-N2-P1B 100.6(1); P1B-N2-P18 83.1(1); C1B-N2-P18 166.9(1). For N3: N3-C12C 1.957(4); N3-C13C 1.939(4); N3-N1C 1.916(3); N3-P1C 2.173(1); N3-C13C-N1C 83.6(2); C1C-N13-C12C 93.2(2); C12C-N13-P1C 100.2(1); P1C-N13-P1C 166.1(1). For N4: N4-C14-N12D 1.958(4); N4-C1D 1.939(4); N4-C1D 1.939(4); N4-P1D 2.162(1); C1D-N4-N1D 84.0(1); C1D-N4-C12D 93.4(2); C12D-N4-P1D 99.8(1); P1D-N4-N1D 82.88(9); C1D-N4-P1D 166.9(1).

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[52] Bruker, APEX2 software, Madison WI, USA, 2014.

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