Redox-Active Pincer Ligands

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 spectrleochemistry, 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 N,N’-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 PONC 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 Rh¹ precursor complexes.[20] We also reported selective reprotonation of the Rh–CPh bond to afford the crystallographically characterized complex [RhCl(CO)(κ²-3-PN-HLCH₂)] with a reprotonated phenyl substituent that is still in the first coordination sphere of Rh¹. 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(κ²-3-PN-C-PONC)] complex and subsequent reprotonation of the nickel–CPh 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)(κ²-3-PN-C-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
for the corresponding Ni–CH₃ complex and the resulting NiᴵᴵΙ species, relevant in the context of C₆H₆–C₃H₅ reductive elimination, may potentially be detectable.²³ Previous reports show that CF₃ ligands can stabilize the NiᴵᴵΙ oxidation state in [Niᴵᴵᴵ(tBu₃tpy)(CF₃)₂]⁺ (tBu₃tpy = 4,4‴,4‴′-tris(tert-butyl)-2,2‴,6,2‴′-terpyridine).²⁴ Reductive elimination from NiᴵᴵΙ would result in formation of a formally Ni¹ 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 Niᴵᴵ–alkyl complexes might lead to the formation of Ni¹ species [Ni¹(alkyl)(κ³-P,N,C-PO₃NC)]⁻ or alternatively to Niᴵ complexes with a radical anionic ligand [Niᴵ(alkyl)(κ³-P,N,C-PO₃NC•⁻)]⁻ 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 Ni¹ coordinated to reduced tpy•⁻, while [Ni(tpy)(X)]⁺ (X = I, Br, Cl) species are best described as Ni¹ 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.

![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 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).](image)
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 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 (Niᴵ/II) oxidation. These redox events, postulated to strongly impact on the oxidation processes, in line with a metal-centered (Niᴵ/II) oxidation 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 [acetylferrocenium]BF₄⁻ ([Fe(η⁵-C₅H₆(CO)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 [Niᴵ(II)(Me)(κ²-P₂N-C⁵-PNC-Me)]⁺ would lead to a Calkyl–CPh bond in a [Niᴵ(II)(κ²-P₂N-P⁵-PNC-Me)]⁺ species with a pendant tolyl group at the phosphino–pyridine ligand. DFT calculations of the EPR parameters for the optimized geometry of solvated Niᴵ complex A, [Niᴵ(NCMe)₂(κ²-P₂N-P⁵-PNC-Me)]⁺ [structure optimized with Turbomole (BP86, def2-TZVP, disp3)] showed good agreement with the experimentally obtained EPR data, using either ORCA or ADF (Figure 2, right). The calculated EPR parameters of the putative oxidized Niᴵᴵ species B, [Niᴵᴵ(II)(II)(NCMe)₂(κ²-P₂N,C-P⁵-PNC-Me)]⁺ 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-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-

![Figure 2](image-url)

**Figure 2.** Left: cyclic voltammograms of a 6 mm solution of 2CH₃ in PrCN/NbBu₄PF₆ at 298 K, with a scan rate of 100 mV/s. Middle: Experimental and simulated X-band EPR spectra of proposedly complex A, [Niᴵ(NCMe)₂(κ²-P₂N-P⁵-PNC-Me)]⁺. The simulated spectrum was obtained using the parameters listed in Table 2. The experimental spectrum was recorded at 30 K in frozen PrCN/MeCN 3:1. Microwave frequency = 9.363973 GHz, modulation amplitude = 4 Gauss, microwave power = 2 mW. Right: Optimized geometry (Turbomole BP86, def2-TZVP, disp3) of the suggested geometry of the Niᴵ complex [Niᴵ(NCMe)₂(κ²-P₂N-P⁵-PNC-Me)]⁺.
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]

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

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(k²-PN-PONC-Me)₂] (B). This species would be formed upon transfer of the ligand from NiⅡ 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 dinitrile silver species B.

Transmetalation of the ligand from NiⅡ to AgⅠ upon C–C reductive elimination was also supported by the rudimentary detection of crystalline [NiⅢ(NCMe)₆](BF₄) (by X-ray diffraction) that separated from the reaction mixture, which may suggest a disproportionation reaction of unstable [NiⅡ(NCMe)₆]BF₄ into a NiⅢ 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 NiⅢ 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 E½ = −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 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$^{\text{II}}$ complex $[\text{Ni}^{\text{II}}\text{Br}(\text{Phbpy})\cdot\cdot\cdot]^-$ (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$^{\text{II}}$ bound to a radical anionic ligand $[\text{Ni}^{\text{II}}(\text{CF}_3)(\kappa^3-P-N-PONC)]^{-}$ rather than a Ni$^{\text{I}}$ 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/$\text{nBu}_4\text{PF}_6$; 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 KC$_8$.

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 $\text{nBu}_4\text{PF}_6$/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 Ni$^{II}$, 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 Ni$^{II}$ complexes containing a radical anionic PONC ligand [Ni$^{II}$(alkyl)(x$^2$-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>Parameter</th>
<th>Exp.[a]</th>
<th>DFT (ORCA)[b]</th>
<th>DFT (ADF)[c]</th>
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<tr>
<td>$g_{iso}$</td>
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<td>2.003</td>
<td>2.003</td>
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<td>$A_{17}^{iso}$</td>
<td>NR</td>
<td>3.3</td>
<td>3.8</td>
</tr>
</tbody>
</table>

[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 Ni$^{II}$-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 [NiII(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 reactive 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 pave a step in this direction.

Conclusions

The four-coordinate nickel–alkyl complexes [Ni(alkyl)(κ3-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 Cαβ-Cβ 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 ([H, 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-T100CV mass spectrometer using field desorption (FD), or JEOL AccuTOF LC, JMS-T100LP mass spectrometer using electron-spray ionization (ESI) or CSI. Complex 1, [NiBr(κ3-PN,C-PONC)] was synthesized as previously reported by us,[22]

[Ni(CH3)(κ3-PN,C-PONC)] (complex 2CH3): Complex 1 (0.080 g, 0.18 mmol) was dissolved in toluene (5 mL) and MeLi (1.6M in Et2O) was added. The reaction was stirred for 5 min, the suspension was filtered through Celite and the solvent evaporated. The product was extracted with n-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, [D3]MeCN, ppm): δ = 7.84 (vt, J = 8.0 Hz, 1 H, Py-CH), 7.56–7.43 (m, 2 H, Ph-CH), 7.34 (d, J = 7.7 Hz, 1 H, Py-CH), 7.20–7.04 (m, 2 H, Ph-CH), 6.82 (d, J = 8.2 Hz, 1 H, Py-CH), 1.45 (d, JCH3 = 14.2 Hz, 18 H, (CH3)2CP), 13.58 ppm. 31P NMR (121 MHz, [D3]MeCN, ppm): δ = 194.28. 13C NMR (75 MHz, [D3]MeCN, ppm): δ = 165.74 (d, JPC = 9.5 Hz, Py-CH), 150.28 (s, Ph-C), 141.79 (s, Py-CH), 134.37 (s, Ph-CH), 130.21 (d, JPC = 5.3 Hz, Ph-CH), 123.09 (d, JPC = 3.5 Hz, Ph-CH), 111.62 (s, Ph-CH), 107.11 (d, JPC = 4.0 Hz, Py-CH), 39.16 (d, JPC = 4.2 Hz, (CH3)2CP). HRMS (CSI): calcd. for C22H31AgN2OP: 477.1225 [M]+; found: 477.1225 [M]+.

[Ni(CF3)(κ3-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 mg in THF) (0.25 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, 92 %, quantitative). Crystals suitable for X-ray analysis were grown by slow evaporation of an Et2O solution. 1H NMR (300 MHz, [D3]MeCN, ppm): δ = 7.73 (s, J = 7.8 Hz, 1 H, Py-CH), 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)2CP). 13C NMR (75 MHz, [D3]MeCN, ppm): δ = 193.40 (d, JPC = 90.7 Hz, 18 H, (CH3)2CP). 13P NMR (121 MHz, [D3]MeCN, ppm): δ = 139.12 (d, JPC = 100.7 Hz, 18 H, (CH3)2CP). HRMS (CSI): calcd. for C20H26F6NiOP: 425.0974; found: 425.1007. 1H NMR (300 MHz, [D3]MeCN, ppm): δ = 13.58 (m, 18 H, (CH3)2CP). 13C NMR (75 MHz, [D3]MeCN, ppm): δ = 162.30 (s, Ph-C), 150.28 (m, Ph-C), 143.22 (s, Ph-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), 127.67 (s, Ph-CH), 112.31 (s, Ph-CH), 37.58–36.58 (m, (CH3)2CP), 27.16 (d, JPC = 10.9 Hz, (CH3)2CP). 20.29 (s, Ph-CH3). One of the Py-CH signals is obscured by the solvent residual signal. HRMS (CSI): m/z calcd. for C22H23AgN2OP: 747.1225 [M]+; found: 747.1248.
Oxidation of 2CF₃: A solution of [thianthrenium]BF₄ (11 μmol, 3.2 mg) in a mixture of PrCN/McCN = 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.

Oxidation of 2CF₃ with [thianthrenium]BF₄ in the presence of AgBF₄: To a Schlenk containing complex 2CF₃ (10 mg, 0.023 mmol), [thianthrenium]BF₄ (7.0 mg, 0.023 mmol) and AgBF₄ (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. Oxidation of 2CF₃ with [thianthrenium]BF₄ in the presence of KC₈ (13 μmol, 1.8 mg) was added to a solution of complex 2CF₃ (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.

Reduction of 2CH₃: K₂C₂F₃ (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: K₂C₂F₃ (11 μmol, 1.5 mg) was added to a solution of complex 2CF₃ (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 NnBu₄NPF₆ (0.1 M) as the supporting electrolyte. Concentration of the analyte: 6 mM. Working electrode: glassy carbon. Counter electrode: Pt coil. Scan rate: 100 mV 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(Oct)Bu₄NPF₆ (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-parameter and reduction measurements were carried out in propionitrile, MeCN or THF, respectively, with N(Oct)Bu₄NPF₆ (0.2 M) as the supporting electrolyte. Working electrode: Pt. Counter electrode: Pt. Reference electrode: Ag wire. Scan rate: 0.003 V s⁻¹.

Computational Details and EPR Property Calculations: Geometry optimizations were carried out with the Turbomole program package[33] coupled to the PQUKs Baker optimizer[34] via the BOPt package[35] at the n-DFT[36]/BP86[37,38] level. We used Grimme’s D3 dispersion corrections (disp3)[39] and the def2-TZVP basis set[40,41] for all atoms, and a small grid (m4). EPR parameters[42,43] were subsequently calculated with the ADF[44–47] 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 code were used, employing unrestricted SPINORBIT ZORA COLLINEAR calculations for the SOC corrected HFI-tensors and Zee-
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[52] Bruker, APEX2 software, Madison WI, USA, 2014.

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