Modular O- vs N-coordination of Pyridylidene Amide Ligands to Iron Determines Activity in Alcohol Oxidation Catalysis

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A family of polydentate pyridine-substituted pyridylidene amide (PYA) complexes bound to iron(II) was developed. Variation of the coordination set from NN-bidentate PYA to tridentate pincer-type pyPYA systems (pyPYA 2 = 2,6-bis(PYA)pyridine) had a large influence on the binding mode to iron(II), including a change from N- to rare O-coordination of the PYA site and a concomitant shift of the predominant ligand resonance structure. These binding mode variations invoke changes in the reactivity of the complexes, which was probed in the peroxide-mediated oxidation of 1-phenylethanol to acetophenone. Comparison with uncomplexed FeCl 2 indicated that bidentate NN coordination is unstable and presumably leads to dissociation of FeCl 2. In contrast, tridentate ligand binding is robust. Remarkably, tridentate PYA pincer coordination inhibits catalytic activity in the NNN binding mode, while ONO coordination greatly enhances catalytic performance. Under optimized conditions, the bis-ligated ONO pincer iron complex [Fe(pyPYA) 2 ][2PF 6 ] reaches full conversion within one hour (0.5 mol% catalyst loading) and under dilute conditions turnover numbers over 20 000 (0.005 mol% catalyst loading).

Introduction

Neutral N-donor ligands are ubiquitous in homogeneous catalysis, including imines, amines, pyridines, and as a more recent addition also pyridylidene amide (PYA) ligands. This latter scaffold has been emerging as promising class of ligands with strong σ-donating properties. Analysis of the PYA’s σ-donor strength has been shown to resemble common C-coordinating N-heterocyclic carbene (NHC) ligands, making them unique nitrogen-based ligands for homogeneous catalysis. PYA consists of a deprotonated amide core bound to an N-alkylated pyridinium ring (Scheme 1). These ligands constitute an overall neutral donor system which is comprised of multiple limiting resonance structures including the neutral imine structure A, and zwitterionic structures B and C. Whereas evidence for resonance structures A and B has been obtained, for example from crystallographic and NMR data, structure C has only been proposed. As a direct result of these multiple resonance structures, the ligand is electronically flexible in its donor properties to metal centers: it can alter between L-type bonding through resonance form A, and X-type metal coordination through resonance form B, and therefore adapt to the influence and requirements of the metal center. Pyridine substituted PYA ligands (Scheme 1, R = 2-pyridine) are related to the more common pyridine-bis-carboxamide ligands. However, the formally neutral nature of PYA ligands and their electronically flexible behavior impart unique properties when compared to the more frequently used dianionic and electronically static pyridine bis-carboxamide systems. For example, the CN-coordinating PYA ligand in complex [Ir(PhPYA)(Cp*)L] adapts its binding mode from a larger contribution of resonance form A when L = Cl to predominantly form B in the solvato complex (L = MeCN) to compensate for the differently charged ligands L (Figure 1). Owing to this electronic flexibility, PYA ligands can stabilize multiple oxidation states on a metal center and their use has brought attractive results to precious metal complexes in homogeneous catalysis (Figure 2), such as Pd(pyPYA)Cl 2 for cross coupling reactions, Ir(PhPYA)(Cp*)Cl for water oxidation and [Ru(bisPYA)(p-cym)Cl]PF 6 for olefin oxidation.

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intermediates of different oxidation states. For example, multidentate nitrogen donor ligands bound to iron have provided attractive catalytic performance for C–H oxidation reactions,15–17 olefin polymerization,18–20 and olefin oxidation.21 Considering these facts, it is remarkable that no PYA ligand has been coordinated to iron. Here, we report the coordination of polydentate PYA ligands to iron and their catalytic activity in oxidation catalysis. Changes in the ligand structure greatly impact the stability, coordination mode, and catalytic activity of the complexes, and reveal evidence for rare O-coordination of these PYA ligands.

Results and discussion

The potentially NN-bidentate coordinating pyridine-substituted PYA ligand (1) was synthesized following previously reported protocols.2,9 Subsequent anion exchange with NH$_4$PF$_6$ in water yielded $^{1}$PF$_6$ (Scheme 2). Coordination of $^{1}$PF$_6$ to FeCl$_2$ was accomplished in a stepwise process including first ligand deprotonation with a stoichiometric amount of LiHMDMS as a strong non-nucleophilic base, followed by addition of the metal precursor, which afforded complex 2 after precipitation with Et$_2$O.13H NMR analysis in CD$_2$CN showed signals ranging from ~50 to ~73 ppm which is consistent with a paramagnetic compound (Figure S5). Magnetic susceptibility measurements using Evans method gave a µ$_{eff}$ of 4.8 for each iron unit indicating a high spin configuration of the d$_{5}$ metal with S = 2.22

In line with this finding, no signal was obtained in the X-band EPR spectrum (solid state and DMSO solution at RT and 77 K). Cyclic voltammetry measurements in MeCN indicate the presence of two oxidative waves at $E_{pa} = 1.16$ and 2.01 V (vs Fe+/Fe, Figure S16 and Table S1). Both oxidations were irreversible under the employed conditions, presumably due to loss of a chloride ligand or complex decomposition. Additionally, stability tests by 1H NMR spectroscopy indicated that the complex is air and moisture sensitive. Exposure of the complex to air directly results in the formation of free ligand and disappearance of the paramagnetic signals, both in the solid state and in solution.

Single crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a MeCN solution under inert conditions, and identified complex 2 as a dimeric structure (Figure 2).23 Each asymmetric unit in the crystal consists of an iron center bound to two nitrogen atoms of the bidentate chelating pyridyl-PYA ligand, and a terminal as well as two bridging chlorido ligands. The C–C bond lengths in the PYA pyridyl ring show bond length alteration, since the C$_6$–C$_8$ is elongated compared to C$_5$–C$_6$ with an average difference of 0.051 Å (Table S4), which indicates some contribution of the diene resonance form A (cf Scheme 1).

![Scheme 2. Synthesis of 2. C$_6$, C$_7$, and C$_8$ are defined in 2.](image)

In an attempt to break this dimer, we explored the addition of stoichiometric amounts of co-ligands, such as 1,2-bis(diphenylphosphino)ethane (dppe), 2,2’-bipyridine (bpy) or ethylenediamine (en), though no reaction was observed. However, stirring the dimer with stoichiometric amounts of NEt$_3$ in THF/pyridine in a 4:1 ratio for several hours and subsequent crystallization of the mixture revealed the formation of small quantities of monomeric complex 3 as a highly air-sensitive complex.24 The molecular structure of 3 was determined by X-ray diffraction analysis, and consists of an octahedral Fe$^0$ center bound to chloride, three pyridine ligands, and the κ$^2$(N,O)-coordinated PYA ligand, implying a rearrangement of the N-binding mode of the amide moiety to the typical O-coordination mode (Figure 3).25 O– instead of N-coordination of the PYA site induces significant changes in the amide unit, with elongation of the C$_6$–O$_1$ bond in 3 compared to 2 (1.272(3) vs 1.229(2) Å) along with a shortening of C$_6$–N$_2$ bond from 1.378(2) Å in 2 to 1.308(3) Å in 3. These bond length changes reflect a more pronounced contribution of the “N=C=O” amide resonance form and indicates an increased relevance of resonance structure C, featuring the formal negative charge located at the oxygen atom (cf Scheme 1). Moreover, complex 3 reveals partial double bond localization in the pyridyl heterocycle. The C$_5$–C$_6$ bonds are elongated compared to C$_9$–C$_7$ with an average difference of 0.048 Å (Table S5). This difference is similar to that observed in complex 2 and suggests that either C–C bond length analysis is not a useful probe to distinguish the
contributions of different resonance structures, or that other resonance structures contribute as well, for example a diene-type structure with the positive and negative charge located on the amide unit (=N=\equiv(C(R)−O−).

Figure 3. ORTEP representation of complex 3 (50% probability ellipsoids; hydrogen atoms and iodide counterion omitted for clarity). Selected bond distances in Å: Fe1−C11: 2.3914(8), Fe1−C1: 2.0927(18), Fe1−N1: 2.189(2), C5−C6: 1.504(4), C7−C8: 1.400(4), C1−C11: 1.405(4), O1−C6: 1.272(3), C8−C9: 1.355(4), C10−C11: 1.354(4), N1−C5: 1.344(4), N2−C6: 1.308(3), N2−C7: 1.377(4), N3−C9: 1.348(4), N3−C10: 1.344(3), N3−C12: 1.474(4). Bond angle O1−Fe1−N1: 75.74(8)°.

Pincer PYA ligands. To increase the stability of the iron PYA complexes, the chelation of the ligand was extended to a tridentate coordinating pincer-type system comprised of a central pyridine unit with two PYA arms derived either from para or ortho aminopyridine (4PPs and 5PPs, Scheme 3).26−28 Complexation of 4PPs was performed by deprotonation of the ligand precursor in the presence of Na2CO3 in DMF, followed by filtration into a DMF solution of FeCl2, which induced precipitation of complex 6 (Scheme 3). The neutral iron(II) complex is paramagnetic as evident from the 1H NMR spectra with shifts in the range of 0 to 73 ppm, and from the magnetic susceptibility of μeff = 4.9 (Evans method), consistent with an S = 2 ground state (Figure S8). Complex 6 shows two quasi reversible and presumably metal-centered redox processes in cyclic voltammetry (Figure S17).29 at E1/2 = −0.46 and −0.31 V (vs Fe+/Fe in DMF). Single crystals suitable for crystallographic analysis were grown by slow diffusion of Et2O into a concentrated solution of the complex in DMSO. The molecular structure of 6 reveals an iron center bound to a \( \kappa^2(N,N,N) \)-coordinated PYA pincer ligand and two chloride ligands, resulting in a five-coordinate trigonal bipyramidal geometry.

In contrast, complexation of the ortho-PYA pincer system 5PPs by the same procedure resulted in the precipitation of bis-pincer iron(II) complex 7. The purple powder is only sparingly soluble in common solvents, including MeCN and DMF, hampering its recrystallization. Analysis by 1H NMR in DMSO-d6 showed that 7 is paramagnetic with shifts ranging from 0 to 70 ppm, and that the complex has only limited stability in this solvent (Figure S9).30 CV analysis of 7 reveals an oxidation at higher potential compared to 6 with E1/2 = −0.25 and −0.05 V (vs Fe/C/Fe in MeCN). Formation of 7 was further supported by HRMS and elemental analysis. Notably, the DMF supernatant from the synthesis of 7 contained traces of a different complex, which crystallized as the mono-pincer complex 8 (Figure S19). This complex might be an intermediate in the formation of the bis-pincer complex, which is the favored product also in related CoII and NiII chemistry.28 In analogy to these cobalt and nickel complexes, the ortho-PYA pincer ligand in the iron(II) complex 8 features a rare O,N,O-tridentate bonding mode, presumably because of a combination of effects including steric shielding of the amide nitrogen by the ortho-substitution, electronic factors associated with the relatively weak donor properties of N-coordinating ortho PYA ligands, as well as the hardness of the 3d metal center.31 While attempts to crystallize complex 7 have failed so far, we speculate that at least one of the pyPYA ligands is bound in the O,N,O-coordination mode based on the structure of 8 and the analogy to other first-row transition metal complexes with this ligand.28

Complexes 6 and 8 are structurally related to anionic pyridine bis-carboxamide complexes such as \([\text{Fe}^{II}(\text{2,6-bis(N-phenylcarbamoyl)pyridine})_2(\text{NEt}_3)](\text{PF}_6)\).32 Generally, these doubly anionic ligands coordinate through the nitrogen atoms, but steric congestion indicated that O-coordination is also feasible.33,34 Bond length analyses in the N-bound para-PYA unit in 6 revealed an average difference of 0.052 Å between Cα−Cβ and Cα−Cγ, suggesting similar double bond localization as noted in complexes 2 and 3 (Table S6). Remarkably, this bond length alteration is just slightly less pronounced in the O-bound ortho-PYA heterocycle of complex 8 (Δd 0.034 Å; Table S7). In addition, the amide C=O bond is only moderately elongated at 1.259(2) Å.
ligand dissociation and release of FeCl

Figure S25 °C), complex

Substituting TBHP by 30% aq. H₂O₂ using only FeCl₃ has comparable reactivity, viz. 0.1 mol% and 25 °C, demonstrates the distinct activity of complex 7.¹¹ Under these conditions, FeCl₂ and complex 2 reached 17 and 18% yield, respectively, after 2 days (entries 6, 7) and complex 6 achieved a modest 6% (entry 8), yet complex 7 accelerated product formation and afforded an appreciable 67% yield within the same time span (entry 9).

Conversions of almost 60% were accomplished at even a lower catalyst loading of 0.05 mol% (entry 10), corresponding to 1960 turnover numbers (TONs). These runs also indicate a considerable rate enhancement compared to FeCl₃.

These catalytic experiments suggest that the bidentate ligand system is not binding strong enough and leads to catalytic activity that is commensurate with ligand dissociation (cf. identical activity of FeCl₃). Unlike the bidentate system, the tridentate pincer-type coordination has a much more profound impact on complex integrity and catalytic activity (see also Table S2 for various control experiments). The NNN coordination mode of the para-PYA pincer ligand in 6 inhibits catalytic activity significantly, suggesting tight bonding of the Fe center within the pincer ligand scaffold, while the bis-pincer coordination pattern in complex 7 imparts a substantially enhanced catalytic performance, presumably after loss of one of the pincer ligands. Even though steric effects cannot be excluded, we surmise that the electronic implication of the PYA resonance structure C with partially anionic oxygen donors beneficially influences the electronic configuration at the iron center to stabilize critical transition states during metal oxidation. In particular, higher oxidation species generated in the reaction of TBHP with the FeII complex are expected to be better stabilized by the ONO-pincer coordination mode due to the high oxophilicity of high-valent iron. This model is supported by catalytic runs in the presence of diphenylamine as an oxygen radical trap aimed at probing the formation of tBuOO⁻ or tBuO⁻ radicals (entry 11).²¹ Under these conditions, product yield dropped to <3% after 24 h, indicating the relevance of oxygen radicals for enabling catalytic turnover and hence indirectly supporting a mechanistic model involving intermediates with Fe in spin-unpaired higher oxidation states.

Since the ortho-PYA pincer iron complex 7 showed the best results throughout, further optimization of the catalytic reaction was performed with this complex. Increasing the reaction temperature to 80 °C resulted in a higher reaction rate and a 91% product yield within 2 h. However, full conversion was not reached due to consumption of the oxidant as observed by ¹H NMR analysis. Adjustment of the protocol therefore included batchwise additions of 1 equiv TBHP at the onset and again after 30 min. This portioned addition afforded 98% conversion after only 1 h using 0.5 mol% of complex 7 (entry 12), compared to a 50% yield with 1 mol% FeCl₃ (entry 13), and

| Entry | [Fe] | Fe loading (mol%) | Temp (°C) | Conversion (time) |
|-------|------|-------------------|-----------|------------------|
| 1     | FeCl₂| 1                 | 50        | 45 (2 h)         |
| 2     | FeCl₂| 1                 | 50        | 33 (2 h)         |
| 3     | FeCl₂| 1                 | 50        | 11 (2 h)         |
| 4     | FeCl₂| 1                 | 50        | 47 (2 h)         |
| 5     | FeCl₂| 0.5               | 50        | 42 (2 h)         |
| 6     | FeCl₂| 0.1               | 25        | 17 (2 d)         |
| 7     | FeCl₂| 0.1               | 25        | 18 (2 d)         |
| 8     | FeCl₂| 0.1               | 25        | 6 (2 d)          |
| 9     | FeCl₂| 0.1               | 25        | 67 (2 d)         |
| 10    | FeCl₂| 0.05              | 25        | 58 (2 d)         |
| 11    | FeCl₂| 0.5               | 50        | <3 (1 h)         |
| 12    | FeCl₂| 0.5               | 80        | 98 (1 h)         |
| 13    | FeCl₂| 1                 | 80        | 50 (1 h)         |
| 14    | FeCl₂| 0.1               | 80        | 1 (1 h)          |
| 15    | FeCl₂| 0.1               | 80        | 5 (1 h)          |
| 16    | FeCl₂| 0.05              | 80        | 92 (24 h)        |

Table 1. Catalytic alcohol oxidation of 1-phenylethanol to acetophenone.⁴

General conditions: iron complex (7 μmol, 1 mol%), MeCN (0.5 mL), 1-phenylethanol (0.7 mmol), TBHP (1.05 mmol), 5 M in decane, Ar atmosphere, yields determined by ¹H NMR spectroscopy (Fig. S10); quantities of substrate and catalyst adjusted for runs with lower catalyst loading, see experimental for details; ⁵0.5 mol% of the dimeric complex was used, to keep [Fe] at 1 mol%; ⁶2 equiv diphenylamine added at the start of the reaction; ⁷TBHP was added in two portions, 1 equiv at t = 0 and 1 equiv at t = 30 min; ⁸1.5 equiv TBHP added in two portions, 1 equiv at t = 0 and 0.5 equiv at t = 20 h.

In contrast, the pincer type complexes 6 and 7 showed diverging reactivities. Complex 6 with a N,N,N-coordinated PYA pincer ligand only yielded 48% product after 24 h (entry 3, cf. >80% for FeCl₃ and complex 2). Complex 7, however, reached full conversion after 24 h and a higher yield at 2 h when compared to 2 (47% vs 33%, entry 4).⁴⁰ Even at 0.5 mol% catalyst loading, 7 accomplishes full conversion after 24 h (entry 5). Comparing the performance at lower catalyst loading and milder temperatures, viz. 0.1 mol% and 25 °C, suggests formation of an identical catalytically active species when starting from 2 or FeCl₃, i.e., catalyst activation of complex 2 presumably involves ligand dissociation and release of FeCl₃ as active entity.
<5% with only the ligand or blank reactions (entries 14, 15, entries S1–S8 in Table S2). The catalytic species shows excellent stability. A catalyst loading as low as 0.005 mol% gave a 92% yield after 24 h and full conversion after 48 h, resulting in over 21 300 TONs (entry 16).\textsuperscript{43} Such high TONs are unusual for iron complexes and are assumed to be a direct consequence of the integrity of the catalytic species due to the rigid tridentate coordination of the PYA pincer ligand combined with the beneficial electronic impact of the ONO donor motif.

The scope of the bis-pincer iron complex 7 in oxidative catalysis was explored with a small variety of distinct substrates (Table 2).\textsuperscript{44} Diphenylmethanol was oxidized quantitatively to benzophenone, indicating that sterically more bulky substrates are converted equally well as 1-phenethanol (entry 1). In contrast, primary alcohols are not selectively transformed to the corresponding aldehyde. For example, benzyl alcohol produces benzaldehyde in reasonable selectivity initially (32% conversion, 78% selectivity to benzaldehyde after 2 h, entry 2), longer reaction times led to full conversion to a mixture of products, however, with only traces of benzaldehyde. Aliphatic alcohols such as cyclohexanol and 4-phenyl-2-butanol were also converted, though yields were only moderate (75% and 53%, respectively) and did not improve upon prolonging the reaction time beyond 5 h (entries 3, 4). Thioethers such as thioanisole were oxidized with high selectivity towards the sulfoxide product with only minute overoxidation to the corresponding sulfone product even after extended reaction periods (98/2 ratio after 20 h, entry 5). Notably, oxidation of pyridine to its N-oxide does not proceed (entry 6), indicating selective oxygen transfer with complex 7 to sulfur but not to nitrogen. This selectivity was further evaluated in the oxidation of 1-(2-pyridyl)ethanol, which afforded exclusively and quantitatively 2-acetylpyridine, demonstrating high preference for alcohol over nitrogen oxidation and no catalyst inhibition by the pyridine functionality (entry 7).

### Table 2. Catalytic oxidation with 7.\textsuperscript{4a}

| Entry | Substrate | Product | % conversion (time) |
|-------|-----------|---------|---------------------|
| 1     |            |         | >99 (1 h)           |
| 2     |            |         | 32 (1 h) (25%)\textsuperscript{b} 98 (24 h) (3%)\textsuperscript{b} |
| 3     |            |         | 69 (3 h) 75 (24 h)  |
| 4     |            |         | 51 (5 h) 53 (24 h)  |
| 5     |            |         | 57 (2 h) 72 (20 h)  |
| 6     |            |         | 0 (1 h) 0 (24 h)    |
| 7     |            |         | >99 (1 h)           |

\textsuperscript{4a} General conditions: iron complex (3 \textmu mol, 0.5 mol%), MeCN (0.5 mL), substrate (0.7 mmol), 1 eq TBHP (0.7 mmol, 5 M in decane) and a second eq TBHP after 30 min, Ar atmosphere, conversions determined by GC analysis or \textsuperscript{1}H NMR spectroscopy. \textsuperscript{b} Spectroscopic yield of benzaldehyde. \textsuperscript{c} Sulfoxide/sulfone ratio 98:2 independent of reaction time.

### Conclusions

In summary, we present the synthesis of the first iron-based PYA complexes having an NN(N) or ONO coordination. The molecular structures reveal the connection between resonance structures and binding mode: the NN(N) coordinating structures have an increased resonance contribution of the diene form, while the zwitterionic resonance structure with a negative charge on the oxygen center is predominant in the ONO complexes. Peroxide-mediated alcohol oxidation provided a useful probe for the integrity of the complexes. While NN-bidentate coordination is too unstable and leads to complex decomposition, N,N,N-tridentate binding results in more rigid iron coordination, yet also to catalytic inhibition. In contrast, O,N,O-tridentate PYA pincer coordination has a positive effect on the stability of the iron complex and its catalytic activity, and this ligand imparts high product yields and excellent TONs. Catalytic oxidation additionally proceeds with sterically more demanding substrates, aliphatic alcohols, and in oxygen transfer oxidation to form sulfoxide, yet leaves imines unaffected. This work highlights the unique coordination flexibility of PYA ligands and their potential to induce attractive catalytic performance with Earth-abundant first row transition metals. Future work will focus on extending the catalytic scope of these iron complexes to other oxidative transformations.

### Experimental section

**General considerations.** All reagents were commercially available and used as received unless specified differently. When specified, reactions were run in an MBRAUN LABmaster 130 argon-filled glovebox. When using inert conditions, chemicals and materials were dried and degassed prior to use. THF, MeCN, hexanes, and Et\textsubscript{2}O were taken from a solvent purification system (SPS), stored over molecular sieves for at least 2 days, degassed with N\textsubscript{2} gas bubbling for 30 min, placed in the glovebox and stored over fresh molecular sieves prior to use. FeCl\textsubscript{2}, ZnCl\textsubscript{2}, NEt\textsubscript{3}, and Na\textsubscript{2}CO\textsubscript{3} were dried under vacuum for 1-2 days before placing them in the glovebox. Mesitylene and 1-phenyl ethanol were placed on molecular sieves in a Schlenk flask, degassed with N\textsubscript{2} bubbling for 30 min, and used under inert N\textsubscript{2} conditions. CD\textsubscript{3}CN and DMSO-d\textsubscript{6} were placed in the glovebox directly, and dried further over molecular sieves. Compounds 1\textsuperscript{1} 4\textsuperscript{27} 5\textsuperscript{28} were synthesized following literature procedures. \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{19}F, and \textsuperscript{31}P NMR spectra were recorded at 25 °C on Bruker spectrometer operating at 300, 75, 282, and 121 MHz, respectively. \textsuperscript{1}H and \textsuperscript{13}C NMR chemical shifts
are reported in ppm relative to SiMe₄ by using the residual solvent resonance as the internal standard. ³¹P NMR chemical shifts are externally referenced to CFC₁₃. ³¹F NMR chemical shifts are externally referenced to CFCl₃. Purity of bulk samples of the complexes has been established by NMR spectroscopy, and when possible by elemental analysis. Elemental analyses were performed at the Department of Chemistry and Biochemistry (DCB), University of Bern, Microanalytic Laboratory using a Thermo Scientific Flash 2000 CHNS-O elemental analyzer. High-resolution mass spectrometry was carried out with a Thermo Scientific LTQ Orbitrap XL (ESI-TOF) by the mass spectrometry group of the DCB. Cyclic voltammograms were recorded using an Autolab PGSTAT1101 from Metrohm in the specified solution solvents: 10 mL solvent, 1 mM sample, and 100 mM tetrabutylammonium hexafluorophosphate (nBu₄N)PF₆ as supporting electrolyte. Solutions were taken under argon from the glovebox. Redox potentials were measured using a glassy carbon working electrode, Ag/AgCl reference electrode (SSCE) and Pt wire auxiliary electrode and are tabulated versus a ferrocene internal standard.⁴⁵ IR spectra were recorded on a Jasco FT/IR 4700 Fourier transform infrared spectrometer.

**Syntheses.**

₁⁹F: In a round bottom flask in air, ¹⁹F (404 mg, 1.18 mmol) was dissolved in water (35 mL) to which a solution of NH₄PF₆ (600 mg, 3.7 mmol) in demi water (10 mL) was added while stirring. The clear colorless solution turned to a white suspension and was stirred for 10 min. The solid was collected by filtration, washed with demi water (2 x 5 mL) and Et₂O (2 x 10 mL) and dried in vacuum, resulting in ₁⁹F as a slightly off-white powder (87%, 370 mg). ¹H NMR (DMSO-δ₆): δH 12.03 (s, 1H, NH), 8.84 (d, J = 4 Hz, 1H, Ar−H), 8.25 (d, J = 7 Hz, 2H, Ar−H), 8.61 (d, J = 7 Hz, 2H, Ar−H), 8.25 (d, J = 8 Hz, 1H, Ar−H), 7.80 (m, 1H, Ar−H), 4.20 (s, 3H, −CH₃). ¹³C NMR (DMSO-δ₆): δC −70.12 (d, JCF = 705 Hz, 1F). ³¹P NMR (DMSO-δ₆): δP −144.2 (s, JPF = 70 Hz, PF₆). ¹³C NMR (DMDO-δ₆): δC 164.80 (Cq), 151.47 (Cq), 148.87 (CH), 148.24 (Cq), 134.95 (CH), 138.61 (CH), 123.59 (CH), 115.91 (CH), 46.49 (CH). IR (cm⁻¹): 3352, 3103, 1719, 1637, 1583, 1515, 1460, 1433, 1282, 1253, 1154, 1113, 1031, 1002. ESI-MS m/z 214.0973, calc: 214.0975.

[Fe(pyPYA)Cl₂](ClO₄)₂ (2): In the glovebox in a 15 mL vial, ¹⁹F (100 mg, 0.30 mmol) was dissolved in THF (1 mL), to which a solution of LiHMDS (59 mg, 0.35 mmol) was added, resulting in an instant color change from orange to dark red. The mixture was stirred for 15 min, after which a solution of FeCl₂ (36 mg, 0.29 mmol) in THF (4 mL) was added. The resulting dark red suspension was stirred for 16 h and the solid was collected by filtration. The product was washed with Et₂O (2 x 3 mL) and hexanes (3 mL) and dried in vacuum to yield the title product as a purple solid (63%, 46.3 mg). ¹H NMR (DMDO-δ₆): δH 73.02, 18.42, 10.88. IR (cm⁻¹): 3041, 1647, 1607, 1582, 1501, 1360, 1334, 1291, 1071, 1034, 876, 858, 524, 446. ESI-MS m/z 473.0119, calc: 473.0103. Elem. anal. calc’d for C₃H₅FeN₂O₂: C 54.54, H 4.02, N 13.97%; found: C 45.82, H 3.51, N 13.88%. Magnetic susceptibility following Evans method was performed in a 95:5 mixture of DMSO-δ₆/DMDO, resulting in a μₐₜ = 4.9, S = 2. Due to the high sensitivity of the compound, no satisfactory elem anal was obtained.

[Fe(pyPYA)Cl(Py)]I (3): In the glovebox in a 15 mL vial, ¹²⁷I (120 mg, 0.35 mmol) was dissolved in THF (2 mL), to which LiHMDS (59 mg, 0.35 mmol) was added, resulting in an instant color change to dark red. The mixture was stirred for 1 h and a solution of FeCl₂ (45 mg, 0.35 mmol) in THF (2 mL) was subsequently added. The resulting dark red suspension was stirred overnight, filtered, and the solids were washed with Et₂O (2 x 3 mL) and hexanes (3 mL) and dried in vacuum, resulting in a brown powder. A part of the product (19.8 mg, 0.03 mmol) was suspended in THF (1 mL). NELu (15.4 mg, 0.06 mmol) in THF (3 mL) was added, and the mixture was stirred for 30 min before pyridine (1 mL) was added. The resulting suspension was stirred for 16 h. The solid was removed by filtration, and the filtrate was crystallized by layering of hexanes over 5 days. The formed crystalline material was collected, washed with Et₂O (3 x 2 mL) and left to dry overnight (applying vacuum leads to product decomposition), resulting in the product as a yellow-to-brown powder in 21% yield (4.2 mg, 6.3 µmol). ¹H NMR (THF/pyridine, crude reaction mixture): δH 6.99 (minor), 58.23, 52.37 (minor), 46.58, 34.17. NMR analysis of the crystalline product was not possible due to instability upon redissolution. IR (cm⁻¹): 3052, 2360, 2028, 1640, 1595, 1572, 1499, 1440, 1385, 1291, 1200, 1145, 1067, 1034, 1006, 891, 812, 755, 698, 522, 485, 456, 421. The quantities were too low and the compound too air-sensitive for elemental analysis.

[Fe(κ⁶NNN-pyPYA)Cl₂] (6): In the glovebox in a 15 mL vial, ⁴²⁷F (100 mg, 0.156 mmol) and Na₂CO₃ (50 mg, 0.479 mmol) were suspended in anhydrous DMF (3 mL). The mixture was stirred for 1 h, after which it was filtered into a solution of FeCl₂ (19.8 mg, 0.156 mmol) in anhydrous DMF (2 mL), resulting in a direct color change from orange to intense purple. The mixture was stirred at room temperature for 16 h, after which it was placed at –50 °C for 1 h. The solution was removed by decantation, and the solids were washed with Et₂O (3 x 4 mL) and dried in vacuum to yield the title product as a intense purple solid (63%, 46.3 mg). ¹H NMR (DMSO-δ₆): δH 73.02, 18.42, 10.88. IR (cm⁻¹): 3041, 1647, 1607, 1582, 1501, 1360, 1334, 1242, 1201, 1103, 1071, 1034, 876, 858, 524, 446. ESI-MS m/z 473.0119, calc: 473.0103. Elem. anal. calc’d for C₉H₁₃Cl₂FeN₂O₂: C 54.54, H 4.02, N 13.97%; found: C 45.82, H 3.51, N 13.88%. Magnetic susceptibility following Evans method was performed in a 95:5 mixture of DMSO-δ₆/DMDO, resulting in a μₐₜ = 4.9, S = 2.

[Fe(κ⁶ONN-pyPYA)Cl₂] (7) and [Fe(κ⁶ONN-pyPYA)Cl₂] (8): Analogues to the synthesis of 6 with the same amounts, using ⁴²⁷F; gave a solid which was washed with MeCN (3 x 3 mL) to yield the title product as a purple solid (49%, 40 mg). ¹H NMR (DMDO-δ₆): δH 70.90, 11.53, 10.83, 7.95. IR (cm⁻¹): 3054, 1628, 1588, 1525, 1497, 1440, 1386, 1297, 1274, 1147, 1066, 952, 839, 780, 756, 729, 685, 495, 427. ESI-MS m/z [M–2Fe]⁺ 375.1064, calc 375.1064. Elem. anal. calc’d for C₁₀H₁₄Fe₂N₂O₂P₂: C 43.86, H 3.29, N 13.46%; found: C 43.81, H 3.20, N 13.57%. Overlaying the decanted DMF solution with Et₂O afforded crystals of compound 8 in small quantities (<5
Representative catalytic procedures. In an argon filled glovebox, a 5 mL Teflon capped microwave reaction vial was loaded with the catalyst (1 mol%, 7 μmol), closed and transferred to a fume hood. While stirring, MeCN (0.5 mL), the substrate (1-phenylethanol, 0.7 mmol), and oxidant (TBHP 5 M in decane, 1.05 mmol) were added consecutively by (micro)syringes. The vial was placed in a heating bath. On set times, 0.05 samples were taken using a 1 mL syringe, diluted in CD$_2$CN (0.4 mL), filtered through a cotton pad, and analyzed by $^1$H NMR spectroscopy. When using an NMR standard, the reaction was performed without sampling. Mesitylene (0.5 eq) was added at the end of the reaction to avoid interference, and a sample was taken and analyzed by NMR spectroscopy as described above. The amounts were adjusted as follows when using lower catalyst loadings: for 0.1 mol% runs: 4 μmol catalyst in 3 mL MeCN with 4 mmol 1-phenylethanol and 6 mmol TBHP; for 0.005 mol% run: 2 μmol catalyst in 3 mL MeCN with 20 mmol 1-phenylethanol and 2 × 20 mmol TBHP.41

Conflicts of interest
There are no conflicts to declare.

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23 Crystallographic data of the complexes reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication numbers 2001555 (2), 2001556 (3), 2001557 (6), 2001558 (7). Details of data collection, structure solution, and refinement are compiled in the ESI.

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