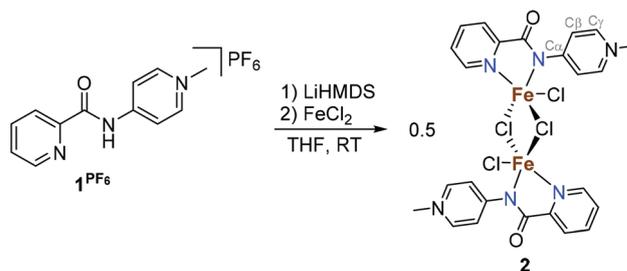


Fig. 1 Selected literature precedents of PYA complexes: [Pd(pyPYA)^R-Cl₂] (R = Me, benzyl), [Ir(PhPYA)(Cp*)L] (L = Cl, MeCN), and [Ru(bisPYA)(*p*-cym)Cl]PF₆.



Scheme 2 Synthesis of **2**. C_α, C_β and C_γ are defined in **2**.

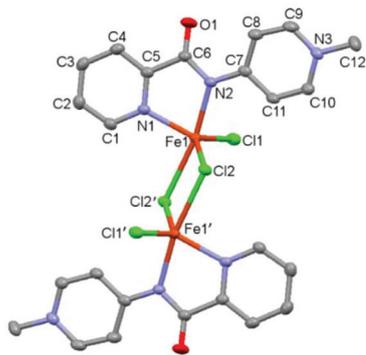


Fig. 2 ORTEP representation of complex **2** (50% probability ellipsoids; hydrogen atoms omitted for clarity). Selected bond distances in Å: Fe1–N1: 2.1142(16), Fe1–N2: 2.1639(15), O1–C6: 1.229(2), N2–C6: 1.361(2), N2–C7: 1.378(2), N3–C9: 1.346(3), N3–C10: 1.354(2), N3–C12: 1.476(2), C5–C6: 1.511(3), C7–C8: 1.418(3), C7–C11: 1.411(3), C8–C9: 1.362(3), C10–C11: 1.365(3). Bond angle N1–Fe1–N2: 78.19(6)°.

Their N-coordination and donor flexibility make PYA ligands particularly attractive for hard and Earth-abundant first row transition metals, offering the opportunity to stabilize catalytic 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 of the rare O-coordination of these PYA ligands.

Results and discussion

The potentially NN-bidentate coordinating pyridine-substituted PYA ligand (**1**¹) was synthesized following previously reported protocols.^{2,9} Subsequent anion exchange with NH₄PF₆ in water yielded **1**^{PF₆} (Scheme 2). The coordination of **1**^{PF₆} to FeCl₂ was accomplished by a stepwise process including first ligand deprotonation with a stoichiometric amount of LiHMDS as a strong non-nucleophilic base, followed by the addition of the metal precursor, which afforded complex **2** after precipitation with Et₂O. ¹H NMR analysis in CD₃CN showed signals ranging from –50 to

+73 ppm which are consistent with a paramagnetic compound (Fig. S5[†]). Magnetic susceptibility measurements performed using the Evans method gave a μ_{eff} of 4.8 for each iron unit indicating a high spin configuration of the d⁶ 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 $E_{\text{pa}} = 1.16$ and 2.01 V (vs. Fc⁺/Fc, Fig. S16 and Table S1[†]). Both oxidations were irreversible under the employed conditions, presumably due to the 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 the free ligand and the disappearance of the paramagnetic signals, both in the solid state and in solution.

Single crystals suitable for X-ray diffraction analysis were grown by the slow evaporation of a MeCN solution under inert conditions, and identified complex **2** as a dimeric structure (Fig. 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_α–C_β bond is elongated compared to the C_β–C_γ bond with an average difference of 0.051 Å (Table S4[†]), which indicates some contribution of the diene resonance form **A** (*cf.* Scheme 1).

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 quantities of NEt₄I in THF/pyridine in a 4 : 1 ratio for several hours and the 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^{II} center bound to chloride, three pyridine ligands, and the κ²(N,O)-coordinated PYA ligand, implying a rearrangement of the N-binding mode of the amide moiety to the untypical O-coordination mode (Fig. 3).²⁵ N-coordination of the PYA site instead of O-coordination induces significant changes in the amide unit, with elongation of the C6–O1 bond in **3** compared to **2** (1.272(3) vs. 1.229(2) Å) along with a shortening of C6–N2



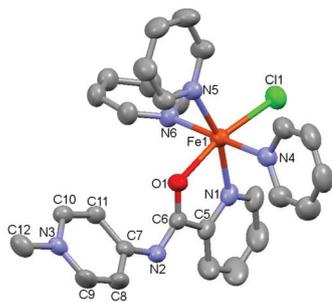
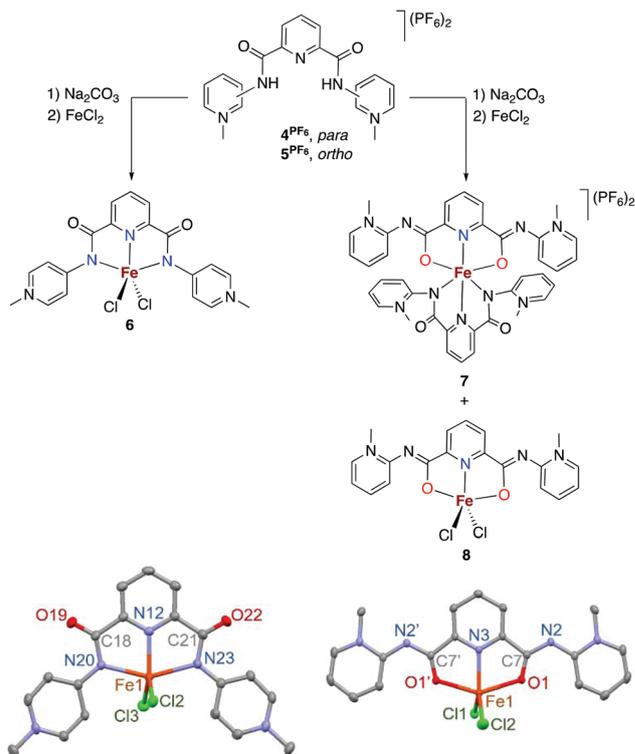


Fig. 3 ORTEP representation of complex **3** (50% probability ellipsoids; hydrogen atoms and iodide counterions omitted for clarity). Selected bond distances in Å: Fe1–Cl1: 2.3914(8), Fe1–O1: 2.0927(18), Fe1–N1: 2.189(2), C5–C6: 1.504(4), C7–C8: 1.400(4), C7–C11: 1.405(4), O1–C6: 1.272(3), C8–C9: 1.355(4), 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)°.

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 indicate the 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 $C_{\alpha}-C_{\beta}$ bonds are elongated compared to the $C_{\beta}-C_{\gamma}$ bonds 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 ($=N^+=C(R)-O^-$).

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 comprising a central pyridine unit with two PYA arms derived either from *para* or *ortho* aminopyridine (4^{PF6} and 5^{PF6} , Scheme 3).^{26–28} Complexation of 4^{PF6} was performed by the deprotonation of the ligand precursor in the presence of Na_2CO_3 in DMF, followed by filtration into a DMF solution of $FeCl_2$, which induced the 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 $\mu_{eff} = 4.9$ (Evans method), consistent with an $S = 2$ ground state (Fig. S8[†]). Complex **6** shows two quasi reversible and presumably metal-centered redox processes in cyclic voltammetry (Fig. S17[†])²⁹ at $E_{1/2} = -0.46$ and -0.31 V (*vs.* Fc^+/Fc in DMF). Single crystals suitable for crystallographic analysis were grown by slow vapor diffusion of Et_2O into a concentrated solution of the complex in DMSO. The molecular structure of **6** reveals an iron center bound to a $\kappa^3(N,N,N)$ -coordinated PYA pincer ligand and two chloride ligands, resulting in a five-coordinate trigonal bipyramidal geometry.



Scheme 3 Synthesis (top) and ORTEP plots (bottom) of complexes **6–8** and ORTEP plots of **6** and **8** shown at 50% thermal ellipsoids, hydrogen atoms and co-crystallized DMSO molecules are omitted for clarity. Selected bond distances in Å: **6**: Fe1–N12: 2.0696(14), Fe1–N20: 2.2476(14), Fe1–N23: 2.2559(14), O19–C18: 1.231(2), O22–C21: 1.233(2), N20–C18: 1.363(2), N23–C21: 1.357(2). **8**: Fe1–N3: 2.109(2), Fe1–O1: 2.1797(12), O1–C7: 1.259(2), N2–C7: 1.329(2).

In contrast, the complexation of the *ortho*-PYA pincer system 5^{PF6} 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. A 1H NMR analysis in DMSO- d_6 showed that **7** is paramagnetic with shifts ranging from 0 to 70 ppm and that the complex has only limited stability in this solvent (Fig. S9[†]).³⁰ A CV analysis of **7** reveals oxidation at higher potential compared to that of **6** with $E_{1/2} = -0.25$ and -0.05 V (*vs.* Fc^+/Fc in MeCN). The 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** (Fig. S19[†]). This complex might be an intermediate in the formation of the bis-pincer complex, which is also the favored product in relation to Co^{II} and Ni^{II} chemistry.²⁸ In analogy to these cobalt and nickel complexes, the *ortho*-PYA pincer ligand in the iron(II) complex **8** features a rare ONO-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 the attempts to crystallize complex **7** have failed so far, we speculate that at least one of the pyPYA₂ ligands is bound in the ONO-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 [Fe^{III}(2,6-bis(*N*-phenylcarbamoyl)pyridine)₂][NEt₄].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 C_α-C_β and C_β-C_γ, 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** (Δ*d* 0.034 Å; Table S7†). In addition, the amide C=O bond is only moderately elongated at 1.259(2) Å (*cf.* 1.232(3) in **6** and 1.272(3) in **3**), while the exocyclic C_{PYA}-N_{amid} bond is shortened to 1.353(2) Å. Together with the contraction of the adjacent C-N bond to 1.329(2) Å (*cf.* 1.360(5) Å in **6**), these data indicate relevant contributions of resonance structures **A** and **C** for complex **8**.

Alcohol oxidation catalysis

We have used catalytic alcohol oxidation as a probe to evaluate the effect of the different ligand coordination modes (Table 1 and Table S2†). Initially, the reactivity of complex **2** was explored in the catalytic oxidation of 1-phenylethanol to acetophenone as a model reaction.³⁵⁻³⁹ Under standard conditions, *viz.* 0.5 mol% of the dimeric iron complex **2**, 1.5 eq. *t*-butyl hydroperoxide (TBHP), 50 °C in MeCN, complex **2** cleanly converted the alcohol to acetophenone and reached full conversion after 24 h, slightly slower than when using only FeCl₂ as the catalyst precursor (Table 1, entries 1,2). Substituting TBHP by 30% aq. H₂O₂ suppressed product formation, which is likely caused by the sensitivity of complex **2** towards water. Under mild conditions (0.1 mol% catalyst at 25 °C), complex **2** and FeCl₂ have comparable reactivity, reaching a product yield of 18 ± 1% after 2 days (entries 6, 7; Fig. S18†). This similar activity suggests the formation of an identical catalytically active species when starting from **2** or FeCl₂, *i.e.*, catalyst activation of complex **2** presumably involves ligand dissociation and the release of FeCl₂ as an active entity.

In contrast, the pincer type complexes **6** and **7** showed diverging reactivities. Complex **6** with an N,N,N-coordinated PYA pincer ligand only yielded 48% product after 24 h (entry 3, *cf.* >80% for FeCl₂ and complex **2**). However, complex **7** reached full conversion after 24 h and resulted in a higher yield at 2 h when compared to **2** (47% *vs.* 33%, entry 4).⁴⁰ Even at a catalyst loading of 0.5 mol%, **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, demonstrates the distinct activity of complex **7**.⁴¹ Under these conditions, FeCl₂ and complex **2** reached 17 and 18% yield, respectively, after 2 days (entries 6,

Table 1 Catalytic alcohol oxidation of 1-phenylethanol to acetophenone^a



Entry	[Fe]	Fe loading (mol%)	Temp. (°C)	Conversion (time)	
1	FeCl ₂	1	50	45 (2 h)	81 (24 h)
2 ^b	2	1	50	33 (2 h)	>99 (24 h)
3	6	1	50	11 (2 h)	48 (24 h)
4	7	1	50	47 (2 h)	>99 (24 h)
5	7	0.5	50	42 (2 h)	>99 (24 h)
6	FeCl ₂	0.1	25	17 (2 d)	
7 ^b	2	0.1	25	18 (2 d)	
8	6	0.1	25	6 (2 d)	
9	7	0.1	25	67 (2 d)	
10	7	0.05	25	58 (2 d)	
11 ^c	7 + Ph ₂ NH	0.5	50	<3 (1 h)	<3 (24 h)
12 ^d	7	0.5	80	98 (1 h)	
13 ^d	FeCl ₂	1	80	50 (1 h)	
14	5 ^{PF₆}	0	80	1 (1 h)	
15	none	0	80	<5 (1 h)	
16 ^e	7	0.005	80	92 (24 h)	98 (48 h)

^a 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. ^b 0.5 mol% of the dimeric complex was used to keep [Fe] at 1 mol%. ^c 2 equiv. diphenylamine added at the start of the reaction. ^d TBHP was added in two portions, 1 equiv. at *t* = 0 and 1 equiv. at *t* = 30 min. ^e 1.5 equiv. TBHP added in two portions, 1 equiv. at *t* = 0 and 0.5 equiv. at *t* = 20 h.

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),⁴² corresponding to turnover numbers (TONs) of 1960. These runs also indicate a considerable rate enhancement compared to FeCl₂.

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 FeCl₂). 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 a 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 the 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

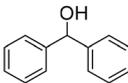
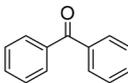
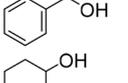
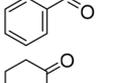
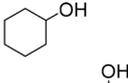
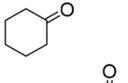
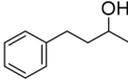
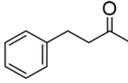
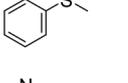
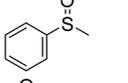
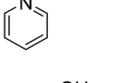
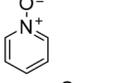
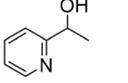
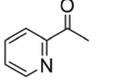


metal oxidation. In particular, higher oxidation species generated in the reaction of TBHP with the Fe^{II} complex are expected to be better stabilized by the ONO-pincer coordination mode due to the high oxophilicity of high-valence iron. This model is supported by catalytic runs in the presence of diphenylamine as an oxygen radical trap aimed at probing the formation of tBuOO• or tBuO• radicals (entry 11).^{21,35} 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 the 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 the consumption of the oxidant as observed by the 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% FeCl₂ (entry 13), and <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 20 000 TONs (entry 16).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).⁴⁴ Diphenylmethanol was oxidized quantitatively to benzophenone, indicating that sterically more bulky substrates are converted equally well as 1-phenylethanol (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) and 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

Table 2 Catalytic oxidation with **7**^a

Entry	Substrate	Product	% conversion (time)	
1			>99 (1 h)	
2			32 (1 h) (25%) ^b	98 (24 h) (3%) ^b
3			69 (3 h) 75 (5 h)	75 (24 h)
4			51 (5 h)	53 (24 h)
5			57 (2 h) ^c	72 (20 h) ^c
6			0 (1 h)	0 (24 h)
7			>99 (1 h)	

^aGeneral conditions: iron complex (3 μmol, 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 ¹H NMR spectroscopy. ^bSpectroscopic yield of benzaldehyde. ^cSulfoxide/sulfone ratio 98:2 independent of reaction time.

2-acetylpyridine, demonstrating high preference for alcohol over nitrogen oxidation and no catalyst inhibition by the pyridine functionality (entry 7).

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, NNN-tridentate binding results in more rigid iron coordination, yet also to catalytic inhibition. In contrast, ONO-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, the chemicals and materials were dried and degassed prior to use. THF, MeCN, hexanes, and Et₂O were taken from a solvent purification system (SPS), stored over molecular sieves for at least 2 days, degassed with N₂ gas bubbling for 30 min, placed in the glovebox and stored over fresh molecular sieves prior to use. FeCl₂, ZnCl₂, NEt₄I, and Na₂CO₃ 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 N₂ bubbling for 30 min, and used under inert N₂ conditions. CD₃CN and DMSO-*d*₆ were placed in the glovebox directly, and dried further over molecular sieves. Compounds **1**^{PF₆}, **4**^{PF₆}, **27** and **5**^{PF₆} (ref. 28) were synthesized following literature procedures. ¹H, ¹³C, ¹⁹F, and ³¹P NMR spectra were recorded at 25 °C using a Bruker spectrometer operating at 300, 75, 282, and 121 MHz, respectively. ¹H and ¹³C 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 85% aqueous H₃PO₄. ¹⁹F NMR chemical shifts are externally referenced to CFCl₃. The purity of the bulk samples of the complexes has been established by NMR spectroscopy, and when possible by elemental analysis. The 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 using a Thermo Scientific LTQ Orbitrap XL (ESI-TOF) by the mass spectroscopy group of the DCB. Cyclic voltammograms were recorded using an Autolab PGSTAT101 from Metrohm in the specified solvent solutions: 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 using a Jasco FT/IR 4700 Fourier transform infrared spectrometer.

Syntheses

1^{PF₆}. In a round bottom flask in air, **1**^I (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 fil-

tration, washed with demi water (2 × 5 mL) and Et₂O (2 × 10 mL) and dried in a vacuum, resulting in **1**^{PF₆} as a slightly off-white powder (87%, 370 mg). ¹H NMR (DMSO-*d*₆): δ_H 12.03 (s, 1H, NH), 8.84 (d, *J* = 4 Hz, 1H, Ar-*H*), 8.80 (d, *J* = 7 Hz, 2H, Ar-*H*), 8.51 (d, *J* = 7 Hz, 2H, Ar-*H*), 8.25 (d, *J* = 8 Hz, 1H, Ar-*H*), 8.16 (td, *J* = 8 Hz, *J* = 1 Hz, 1H, Ar-*H*), 7.80 (m, 1H, Ar-*H*), 4.20 (s, 3H, -CH₃). ¹⁹F NMR (DMSO-*d*₆): δ_F -70.12 (d, *J*_{FP} = 705 Hz, 1F). ³¹P NMR (DMSO-*d*₆): δ_P -144.2 (s, ²*J*_{PF} = 710 Hz, PF₆). ¹³C NMR (DMSO-*d*₆): δ_C 164.80 (Cq), 151.47 (Cq), 148.87 (CH), 148.24 (Cq), 145.94 (CH), 138.61 (CH), 128.31 (CH), 123.59 (CH), 115.91 (CH), 46.49 (CH₃). 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]₂ (**2**). In the glovebox in a 15 mL vial, **1**^{PF₆} (100 mg, 0.30 mmol) was dissolved in THF (1 mL) to which a solution of LiHMDS (48 mg, 0.29 mmol) in THF (3 mL) 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 × 3 mL) and hexanes (3 mL) and dried in a vacuum to afford **2** as a dark red highly air-sensitive powder (84 mg, 86%). ¹H NMR (CD₃CN): δ_H 73.13, 64.25 (minor), 54.51, 9.88, 8.04, 4.02, 0.02, -15.83, -50.21. IR (cm⁻¹): 3052, 1646, 1589, 1499, 1334, 1249, 1200, 1128, 1046, 1019, 912, 839, 755, 695, 556, 468. Magnetic susceptibility following the Evans method was performed in a 50 : 1 mixture of DMSO-*d*₆/DMSO, resulting in a μ_{eff}: 4.9, *S* = 2. Due to the high sensitivity of the compound, no satisfactory elemental analysis was performed.

[Fe(pyPYA)Cl(Py)₃]I**** (**3**). In the glovebox in a 15 mL vial, **1**^I (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 × 3 mL) and hexanes (3 mL) and dried in a vacuum, resulting in a brown powder. A part of the product (19.8 mg, 0.03 mmol) was suspended in THF (1 mL). NEt₄I (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 × 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): δ_H 69.09 (minor), 58.23, 52.37 (minor), 46.58, 34.17. NMR analysis of the crystalline product is not possible due to instability upon redissolution. IR (cm⁻¹): 3052, 2360, 2028, 1640, 1595, 1572, 1527, 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.



$[\text{Fe}(\kappa^{\text{NNN}}\text{-pyPYA}_2)\text{Cl}_2]$ (**6**). In the glovebox in a 15 mL vial, 4^{PF_6} (100 mg, 0.156 mmol) and Na_2CO_3 (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 FeCl_2 (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 Et_2O (3×4 mL) and dried in a vacuum to yield the title product as an intense purple solid (63%, 46.3 mg). ^1H NMR ($\text{DMSO-}d_6$): δ_{H} 73.02, 18.42, 10.88. IR (cm^{-1}): 3041, 1647, 1607, 1582, 1501, 1360, 1334, 1242, 1201, 1133, 1071, 1031, 940, 847, 765, 689, 524, 446. ESI-MS m/z 473.0119, calc: 473.0103. Elem. anal. calcd for $\text{C}_{19}\text{H}_{17}\text{Cl}_2\text{FeN}_5\text{O}_2 \times 1.5\text{H}_2\text{O}$: C 45.54, H 4.02, N 13.97%; found: C 45.82, H 3.51, N 13.88%. Magnetic susceptibility following the Evans method was performed in a 95 : 5 mixture of $\text{DMSO-}d_6/\text{DMSO}$, resulting in a μ_{eff} : 4.9, $S = 2$.

$[\text{Fe}(\text{pyPYA}_2)_2](\text{PF}_6)_2$ (**7**) and $[\text{Fe}(\kappa^{\text{ONO}}\text{-pyPYA}_2)\text{Cl}_2]$ (**8**). Analogues to the synthesis of **6** with the same amounts, using 5^{PF_6} , gave a solid which was washed with MeCN (3×3 mL) to yield the title product as a purple solid (49%, 40 mg). ^1H NMR ($\text{DMSO-}d_6$): δ_{H} 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 $[\text{M}-2\text{PF}_6]^{2+}$ 375.1064, calc 375.1046. Elem. anal. calcd for $\text{C}_{38}\text{H}_{34}\text{F}_{12}\text{FeN}_{10}\text{O}_4\text{P}_2$: 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 Et_2O afforded crystals of compound **8** in small quantities (<5 mg). ESI-MS m/z $[\text{M}]^+$ 473.0118, calc: 473.0103; $[\text{M} - \text{Cl}]^+$ 438.0430, calc: 438.0415.

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 mL samples were taken using a 1 mL syringe, diluted in CD_3CN (0.4 mL), filtered through a cotton pad, and analyzed by ^1H 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 of MeCN with 20 mmol 1-phenylethanol and 2×20 mmol TBHP.⁴³

Conflicts of interest

There are no conflicts to declare.

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