

Redox Noninnocent Azo-Aromatic Pincers and Their Iron Complexes. Isolation, Characterization, and Catalytic Alcohol Oxidation

Suman Sinha,[†] Siuli Das,[†] Rina Sikari,[†] Seuli Parua,[†] Paula Brandaõ,[‡] Serhiy Demeshko,[§] Franc Meyer,[§] and Nanda D. Paul*,^{†©}

[†]Department of Chemistry, Indian Institute of Engineering Science and Technology, Shibpur, Botanic Garden, Howrah 711103, India [‡]Departamento de Química/CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

[§]Universität Göttingen, Institut für Anorganische Chemie, Tammannstrasse 4, D-37077 Göttingen, Germany

S Supporting Information

ABSTRACT: The new redox-noninnocent azoaromatic pincers 2-(arylazo)-1,10-phenanthroline (L¹) and 2,9-bis(phenyldiazo)-1,10-phenanthroline (L^2) are reported. The ligand L^1 is a tridentate pincer having NNN donor atoms, whereas L² is tetradentate having two azo-N donors and two N-donor atoms from the 1,10-phenanthroline moiety. Reaction of $FeCl_2$ with L¹ or L² produced the pentacoordinated mixed-ligand Fe(II) complexes FeL^1Cl_2 (1) and FeL^2Cl_2 (2), respectively. Homoleptic octahedral Fe(II) complexes, mer- $[Fe(L^1)_2](ClO_4)_2$ [3](ClO₄)₂ and mer- $[Fe(L^2)_2](ClO_4)_2$ [4](ClO₄)₂, have been synthesized from the reaction of hydrated $Fe(ClO_4)_2$ and L^1 or L^2 . The ligand L^2 , although having four donor sites available for coordination, binds the iron center in a tridentate fashion with one uncoordinated pendant azo function. Molecular and electronic structures of the isolated complexes have been scrutinized thoroughly by various spectroscopic techniques, single-crystal X-ray crystallography, and density functional theory. Beyond mere characterization, complexes 1 and 2 were successfully used as catalysts for the aerobic oxidation of primary and secondary benzylic alcohols. A



wide variety of substituted benzyl alcohols were found to be converted to the corresponding carbonyl compounds in high yields, catalyzed by complex 1. Several control reactions were carried out to understand the mechanism of this alcohol oxidation reactions.

INTRODUCTION

The chemistry of redox-noninnocent ligands, particularly when they are coordinated to transition-metal ions, has been an active area of research over the years.¹ Redox-noninnocent ligands are often found to play crucial roles in important natural processes mediated by metalloenzymes.² This class of ligands not only offers binding to the metal ions but also can participate in electron transfer processes. Over the decades the main research in this area was focused on understanding the ambiguous electronic structure and bonding of such complexes. However, recently, employing the redox-active nature of these ligands, increasing efforts are devoted to the use of these complexes to bring about useful chemical transformations, catalysis in particular.³ Other than catalytic applications, the ligandcentered redox events have also found several useful applications in molecular electronics as well.⁴

Therefore, the design and synthesis of new redox-noninnocent ligands having multifunctional properties are of immense interest. Among the various redox noninnocent ligands available, the chemistry of the diamine and aminophenol ligand systems has been studied extensively.⁵ In recent years, several new ligands were designed and synthesized with the basic diamine/aminophenol part kept intact.⁶ The diimine types of ligands have also been of particular interest in recent times due to their rich redox chemistry as well as extensive catalytic applications. Chirik and co-workers explored several unusual chemical transformations using base metal (particularly Fe and Co) complexes of 2,6-bis(arylimino)pyridine where the ligand-centered redox events play a crucial role during catalytic turnover.⁷ In contrast, the chemistry of azo-aromatic ligands has been less explored, although their redox-noninnocent character has been known for some time. The presence of low-lying π^* orbitals makes this class of ligands susceptible toward reduction, which indeed confers the ability to act as an electron sink during catalytic turnover.

Kaim and co-workers made a significant contribution to this field with various azo-aromatic ligands, particularly with the 2,2'-azobipyridine ligand system.⁸ On the other hand, Goswami and co-workers extensively studied the chemistry of 2-

Received: August 31, 2017

(arylazo)pyridine and related ligand systems.⁹ A few other groups also studied the coordination chemistry of some further azo-aromatic ligands.¹⁰ However, unlike with the diamine/ aminophenol ligand systems, the chemistry with redox-active azo-aromatics has been mainly limited to studies of structure– bonding relationships.^{8–10} There are only a few reports or attempts known where azo-aromatic ligands were exploited to perform catalytic reactions utilizing the redox-active nature of the azo chromophore. Recently, in a seminal work Goswami and co-workers reported the synthesis of the tridentate azo-aromatic pincer 2,6-bis(phenylazo)pyridine, and they have successfully used its nickel complexes for catalytic alcohol oxidation reactions where the azo-aromatic ligand acts as an electron reservoir during catalytic turnover.¹¹

Herein we introduce the two new redox noninnocent azoaromatic scaffolds 2-(arylazo)-1,10-phenanthroline (L^1) and 2,9-bis(phenyldiazo)-1,10-phenanthroline (L^2) with the aim of developing new azo-aromatic ligand-based catalysts for bringing about useful chemical transformations (Figure 1). The ligand



Figure 1. Ligands introduced in this paper.

L¹ is a tridentate pincer having NNN donor atoms, whereas L² is a tetradentate ligand having two azo-N donors and two Ndonor atoms from the 1,10-phenanthroline moiety. Other than the synthesis of the ligands, as a first report, their coordination chemistry with ferrous salts will be described. The ligands along with their Fe complexes have been characterized thoroughly using different spectroscopic techniques in combination with density functional theory (DFT) studies. Beyond mere characterization, to explore some first catalytic applications, catalytic alcohol oxidation reactions were chosen because of their relevance to chemical energy conversion using renewable resources.¹² Interestingly, the pentacoordinated Fe complexes 1 and 2 showed excellent catalytic activity in the oxidation of both primary and secondary benzylic alcohols.

RESULTS AND DISCUSSION

Synthesis. The ligands L^1 and L^2 were synthesized via the condensation of nitrosobenzene with the corresponding amino-1,10-phenanthrolines under highly alkaline conditions. Reaction of 2-amino-1,10-phenanthroline with nitrosobenzene in a 1:1 molar ratio produced the ligand L^1 in nearly 70% yield, whereas coupling of 2,9-diamino-1,10-phenanthroline with nitrosobenzene gave L^2 in 60% yield. Amino-1,10-phenanthrolines were synthesized following an available literature procedure.¹³ After initial workup followed by chromatographic purification, the identity of the newly synthesized orange ligands was confirmed by electrospray ionization (ESI) mass spectrometry. It showed an intense peak originating from the molecular ion $[L^{1b} + H]^+$ at m/z = 319 amu and $[L^2 + H]^+$ at m/z = 389 amu,

respectively. The experimental spectral features of the ligands correspond well to the simulated isotopic pattern for the given formulations. The representative spectrum of $[L^{1b}+H]^+$ along with its simulated pattern are shown in the Figures S1 and S2 in the Supporting Information. The $^1\mathrm{H}$ NMR spectra of $L^{1a,b}$ and L^2 are displayed in Figures S3–S5 in the Supporting Information.

After successful characterization of the ligands, their coordination behavior was explored with some chosen iron salts. The reaction of $L^{1a,b,2}$ (0.17 mmol) with FeCl₂ (0.17 mmol) produced the new, air-stable brown neutral complexes [Fe($L^{1a,b}$)Cl₂] (1a,b) and [Fe(L^2)Cl₂] (2) in nearly 90% yield (Scheme 1). On the other hand, the reaction of $L^{1a,b,2}$ with

Scheme 1. Synthesis of the Iron Complexes

FeCl ₂	+	$L^1 \xrightarrow{\text{EtOH, Reflux}} 4 \text{ h}$	$[FeL^{1}Cl_{2}]$ ([1]; L ¹ = L ^{1a} [1a], L ¹ = L ^{1b} [1b])
FeCl ₂	+	$L^2 \xrightarrow{\text{EtOH, Reflux}} 4 \text{ h}$	[FeL ² Cl ₂] [2]
Fe(ClO ₄) ₂ .6H ₂ O	+	$L^1 \xrightarrow{\text{EtOH, Reflux}} 4 \text{ h}$	$[Fe(L^1)_2](ClO_4)_2$ ([3](ClO ₄) ₂ ; $L^1 = L^{1a}$ ([3a](ClO ₄) ₂),
Fe(ClO ₄) ₂ .6H ₂ O	+	$L^2 \xrightarrow{\text{EtOH, Reflux}} 4 \text{ h}$	$L^{1} = L^{1b} ([3b](ClO_{4})_{2})$ [Fe(L ²) ₂](ClO ₄) ₂ [4](ClO ₄) ₂

hydrated $Fe(ClO_4)_2$ yielded the dicationic green air-stable complexes $[Fe(L^{1a,b})_2](ClO_4)_2$ $([3a](ClO_4)_2$, $[3b](ClO_4)_2)$ and $[Fe(L^2)_2](ClO_4)_2$ ([4](ClO₄)₂) in nearly 80% yield. Elemental analysis along with positive-ion ESI mass spectra of these complexes convincingly support their formulations (see the Supporting Information). For example, complex 1a showed an intense peak due to the molecular ion $[1a]^+$ at m/z = 409amu. Notably, the experimental spectral features of the complexes correspond well to the simulated isotopic pattern for the given formulation. A representative spectrum, that of 1a along with the simulated spectrum, is shown in Figure S9 in the Supporting Information. Complexes 1 and 2 have been found to be paramagnetic in nature. The room-temperature magnetic moment μ_{eff} of complex 1a is 4.96 μ_{B} , while that of 2 is 4.97 μ_{B} . These experimental findings indeed indicate the presence of high-spin Fe(II) ions. On the other hand, complexes [3a]- $(\tilde{ClO}_4)_2$, $[3b](ClO_4)_2$, and $[4](ClO_4)_2$ possess an $\tilde{S} = 0$ ground state, as determined by magnetic susceptibility measurements at room temperature. Complexes $[3a](ClO_4)_2$ and $[3b](ClO_4)_2$ showed sharp ¹H NMR signals in the normal range of diamagnetic compounds; the coordinated ligands were found to be magnetically equivalent on the NMR time scale (Figure S12 in the Supporting Information). However, the observation of multiple overlapping signals in the ¹H NMR spectrum of $[4](ClO_4)_2$ points to a different coordination mode of the two azo chromophores in L^2 , which was confirmed later by an X-ray structure determination (Figure S15 in the Supporting Information).

X-ray Crystallography. The newly synthesized ligand L^{1a} and the iron complexes have been characterized by X-ray diffraction. Crystallographic parameters are collected in Table 1.

The free base ligands, L^1 and L^2 , are semisolid at room temperature, but X-ray diffraction (XRD) quality single crystals could be obtained for the perchlorate salt of L^{1a} by slow

Table 1. Summary of Selected Experimental and Calculated Bond Lengths (Å) and Bond Angles (deg) of L^{1a} , $[L^{1a}]^{\bullet-}$, $[L^{1a}]^{2-}$, L^2 , $[L^2]^{\bullet-}$, $[L^2]^{\bullet-2-}$, 1a, 2, $[3a]^{n+}$, and $[4]^{n+}$ (n = 0-3)

		Fe-N1	Fe-N3	Fe-N4	N1-N2	N1-Fe-N3	N3-Fe-N4
[HL ^{1a}]ClO ₄	X-ray				1.267(3)		
	DFT				1.27547		
$[\mathbf{L}^{1a}]^{ullet-}$	DFT				1.34088		
$[L^{1a}]^{2-}$	DFT				1.37861		
L^2	DFT				1.27823		
$[L^2]^{\bullet-}$	DFT				1.31328		
$[L^2]^{\bullet \bullet 2-}$	DFT				1.35962		
1a	X-ray	2.149(1)	2.031(1)	2.269(1)	1.290(2)	72.35(4)	74.24(4)
	DFT	2.53472	2.14537	2.27992	1.26492	75.27154	67.26568
2	X-ray	2.225(2)	2.046(2)	2.255(2)	1.276(3)	70.75(3)	74.14(7)
	DFT	2.54879	2.16204	2.28989	1.26408	66.848	74.642
[3a] ³⁺	DFT	2.12834	1.89847	2.08110	1.28450	75.835	80.692
$[3a]^{2+}$	X-ray	1.980(4)	1.875(4)	2.054(4)	1.288(6)	76.1(2)	80.4(2)
	DFT	2.11694	1.89826	2.09471	1.28232	75.851	80.265
$[3a]^+$	DFT	2.0612	1.89448	2.09848	1.31373	76.377	80.009
[3a]	DFT	2.03934	1.89634	2.10891	1.34234	76.844	79.579
[4] ³⁺	DFT	2.09830	1.89543	2.13203	1.27797	76.443	80.227
[4] ²⁺	X-ray	1.953(4)	1.854(3)	2.053(4)	1.300(5)	77.0(2)	80.1(1)
	DFT	2.10475	1.89632	2.13429	1.27783	76.252	79.673
[4] ⁺	DFT	2.00960	1.89456	2.22246	1.32754	77.902	78.055

evaporation of an acetonitrile solution of L^{1a} containing a drop of perchloric acid. An ORTEP view of the molecular structure of the cation of HL^{1a} ·ClO₄ is shown in Figure 2. The X-ray



Figure 2. ORTEP view of L^{1a} -H with ellipsoids at the 50% probability level. The ClO₄- counterion and hydrogen atoms are omitted for clarity.

structure indeed confirms the formation of the new planar azoaromatic pincer L^{1a} . It shows a trans geometry about the diaza chromophore. The N–N distance is 1.267(3) Å, indicative of a double bond.

Single crystals of complex **1b** were obtained by slow evaporation of its solution in a dichloromethane—hexane solvent mixture. An ORTEP view of the molecular structure of complex **1b** with partial atom numbering scheme is displayed in Figure 3. The geometry of the complex was found to be intermediate between ideal trigonal-bipyramidal and squarepyramidal geometry with a calculated τ (index of trigonality) value of 0.50 (for an ideal trigonal-bipyramdal geometry $\tau = 1$ and for an ideal square-pyramidal geometry $\tau = 0$). Two Ndonor atoms N1(azo) and N4(phen) occupy the apical positions with a N1–Fe–N4 angle of 145.15°. The N–N bond length in the coordinated ligand was found to be slightly elongated at 1.290(2) Å in comparison to the free ligand



Figure 3. ORTEP view of $FeL^{1b}Cl_2$ (1b) with ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

(1.267(3) Å). Notably, in similar systems, N–N distances are considered to be an excellent indicator of the charge and the oxidation state of the coordinated ligand.^{8,9} The N–N bond elongation sometimes reported to occur because of $d\pi$ (metal) $\rightarrow \pi^*(L)$ back-bonding interactions and in some cases complete transfer of an electron to the π^* orbital of the ligand, producing an azo-anion radical, was also found to be responsible. Therefore, elongated N–N bonds in coordination complexes always lead to ambiguity with respect to the oxidation state formalism. In complex 1b, the elongated N–N bond indeed leads to two different limiting electronic structure possibilities, $[Fe^{II}(L^{1b})Cl_2]$ and $[Fe^{III}(L^{1b})^{\bullet-}Cl_2]$; as will be described below, the situation was clarified using different spectroscopic techniques combined with DFT studies.

X-ray-quality crystals for complex 2 were obtained via the slow diffusion of its dichloromethane solution into hexane. An ORTEP view of the molecular structure of complex 2 with partial atom numbering scheme is displayed in Figure 4. The X-ray structure confirms the formation of the new tetradentate ligand L^2 and formation of its Fe complex having the molecular



Figure 4. ORTEP view of FeL^2Cl_2 (2) with ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

formula $[FeL^2Cl_2]$. The metal ion in complex 2 is pentacoordinated. The τ value was calculated to be 0.18. This value is intermediate between trigonal-bipyramidal and squarepyramidal geometry and is closer to the latter (ideal $\tau = 0$). The ligand L² binds the central Fe center in a tridentate fashion with one uncoordinated pendant azo chromophore. The two Ndonor atoms N1(azo) and N4(phen) occupy the apical positions with an N1–Fe–N4 angle of 143.47°. Complex 2 shows two distinct N–N bond lengths; the azo chromophore coordinated to the Fe center was found to be elongated (1.276(3) Å), whereas the uncoordinated chromophore has a N–N distance of 1.253(2) Å.

Single crystals of complex $[3b](ClO_4)_2$ suitable for X-ray diffraction were obtained by slow diffusion of its acetonitrile solution into toluene. An ORTEP view of the molecular structure of complex $[3b](ClO_4)_2$ with partial atom numbering scheme is displayed in Figure 5. The molecular structure of complex $[3b](ClO_4)_2$ consists of one $[Fe(L^{1b})_2]^{2+}$ cation and two perchlorate anions, leading to the molecular formula $[Fe^{II}(L^{1b})_2](ClO_4)_2$. The geometry of the cation $[3b]^{2+}$ is a distorted octahedron comprising two meridionally coordinating ligands. The presence of an approximate (noncrystallographic) C_2 axis makes half of the molecule identical with the other half,



Figure 5. ORTEP view of $[Fe(L^{1b})_2](ClO_4)_2$ ([**3b**](ClO₄)₂) with ellipsoids at the 50% probability level. The ClO_4^- counterions and hydrogens are omitted for clarity.

in accordance with ¹H NMR spectroscopic solution studies. The N–N distances were found to be 1.288(6) and 1.282(6) Å, respectively. Given the diamagnetic nature of complex $[3]^{2+}$ as revealed from room-temperature magnetic susceptibility measurements and ¹H NMR analysis, the N–N bond elongation was ascribed to $d\pi(Fe^{II}) \rightarrow \pi^*(L^1)$ back-bonding interactions. The other limiting electronic structure possibilities, $[Fe^{IV}{(L^1)^{\bullet-}}_2]^{2+}$ and $[Fe^{III}(L^1)^{\bullet-}(L^1)]^{2+}$ with S = 0 ground state, both having elongated N–N distances, however, could not be excluded at this point on the basis of X-ray crystallographic characterization. However, ⁵⁷Fe Mössbauer spectroscopic analysis along with DFT studies indeed are in agreement with the closed-shell singlet $(S = 0) [Fe^{II}(L^{1a,b})_2]^{-}$ (ClO₄)₂ electronic structure description (cf. below).

Single crystals of complex $[4](ClO_4)_2$ were obtained by slow evaporation of its solution in an acetonitrile-toluene solvent mixture. The molecular structure of complex $[4](ClO_4)_2$ consists of one $[Fe(L^2)_2]^{2+}$ cation and two perchlorate anions, leading to the molecular formula $[Fe^{II}(L^2)_2](ClO_4)_2$ (Figure 6).



Figure 6. ORTEP view of $[Fe(L^2)_2](ClO_4)_2$ ([4](ClO₄)₂) with ellipsoids at the 50% probability level. The ClO_4^- counterions and hydrogens are omitted for clarity.

Two tetradentate ligands L^2 bind to the central Fe ion in a tridentate meridional fashion, yielding a distorted-octahedral geometry with one uncoordinated pendent azo chromophore from each ligand. Complex $[4]^{2+}$ also possesses an approximate (noncrystallographic) C_2 axis of symmetry. The coordinated azo chromophores were found to be slightly elongated (N–N = 1.300(5) Å), whereas the uncoordinated pendent azo chromophores have N–N distances of 1.248(6) Å.

Magnetic Susceptibility Measurements and Mössbauer Spectroscopy. To confirm the spin states and to study the magnetic properties of the new Fe complexes, variabletemperature magnetic susceptibility measurements were performed on polycrystalline samples of 1b and $[3b](ClO_4)_2$ in the temperature range 2-295 K. The temperature dependence of the magnetic behavior ($\chi_{\rm M}T$ versus T plot, $\chi_{\rm M}$ being the molar magnetic susceptibility) is shown in Figure 7. At 295 K, the value of the product $\chi_{\rm M} T$ (3.08 cm³ mol⁻¹ K) for 1b is close to the spin-only value for high-spin Fe(II) with an S = 2 ground state (3.00 cm³ mol⁻¹ K). As shown in Figure 7, $\chi_{\rm M}T$ remains almost unaltered in the temperature range 55-295 K; however, below 50 K $\chi_{\rm M}T$ starts decreasing and reaches a limiting low-temperature value of 0.54 $\text{cm}^3 \text{ mol}^{-1}$ K at 2 K. Modeling of the experimental data using an appropriate spin Hamiltonian for zero-field splitting and Zeeman interaction and including a term for temperature-independent paramagnetism (TIP) provided the values g = 2.02, |D| = 15.2 cm⁻¹, and TIP =



Figure 7. $\chi_{\rm M}T$ vs T plot of 1b (circles, black) and [3b](ClO₄)₂ (circles, red, bottom). The solid lines represent the best fits (see text for details).

8.2 × 10⁻⁴ cm³ mol⁻¹. For [**3b**](ClO₄)₂, $\chi_M T$ remains close to zero over the whole temperature range (0.05 cm³ mol⁻¹ K in the range 25–295 K) and can be simulated by assuming a small amount of paramagnetic impurity (1.2%, S = 5/2) and TIP (3.7 × 10⁻⁴ cm³ mol⁻¹). These experimental data are indeed consistent with the diamagnetic nature of complex [**3b**](ClO₄)₂ as revealed by ¹H NMR spectral analysis.

To get a closer look at the electronic structures and oxidation state assignments of these Fe complexes, zero-field 57Fe Mössbauer spectroscopic analyses were also carried out on the polycrystalline samples of 1b and $[3b](ClO_4)_2$. At 80 K the spectrum of **1b** shows a doublet with isomer shift $\delta = 0.62 \text{ mm}/$ s and quadrupole splitting $\Delta E_Q = 1.87 \text{ mm/s}$ (Figure 8). The isomer shift is somewhat lower than typical values for fivecoordinate high-spin Fe(II) complexes but can be explained by the strong π -acceptor nature of the ligand system, similar to the findings for related systems reported by Goswami and coworkers.9c The even lower value of the isomer shift of 1b in comparison to the similar Fe(II) complexes FeL^{3,4}Cl₂ (L³ = 2,6-bis(arylimino)pyridine; $L^4 = 2,6$ -bis(arylazo)pyridine) may be attributed to the enhanced $d\pi(\text{metal}) \rightarrow \pi^*(L)$ backdonation in the case of 1b.9c,14 The quadrupole doublet of 1b at 80 K is slightly asymmetric. Interestingly, the asymmetry effect is temperature dependent (a broader spectrum can be observed

at 7 K, whereas at 200 K the asymmetry almost vanishes; see the Supporting Information) and, therefore, it can be attributed to the spin-lattice relaxation. At 80 K complex $[3b](ClO_4)_2$ shows a doublet with isomer shift $\delta = 0.22$ mm/s and quadrupole splitting $\Delta E_Q = 1.80$ mm/s, typical for low-spin Fe(II) ions.^{9c,15} Other electronic structure possibilities such as $[Fe^{IV}\{(L^1)^{\bullet-}\}_2]^{2+}$ and $[Fe^{III}(L^1)^{\bullet-}(L^1)]^{2+}$, having either lowspin Fe(IV) or low-spin Fe(III) centers coupled antiferromagnetically with ligand radicals, would have a much lower isomer shift or much larger quadrupole splitting, respectively.

Cyclic Voltammetry and EPR Spectroscopy. Cyclic voltammograms of $L^{1a,b}$, L^2 , **1a**, **1b**, **2**, $[3a](ClO_4)_2$, $[3b]-(ClO_4)_2$, and $[4](ClO_4)_2$ were recorded in CH₃CN solutions containing 0.1 M [Bu₄N]ClO₄ at 25 °C; potentials are referenced to the saturated Ag/AgCl electrode. The results are summarized in Table 2. The voltammograms for L^{1b} , L^2 , $[3a](ClO_4)_2$, and $[4](ClO_4)_2$ are displayed in Figure 9, and those of **1a** and **2** are shown in Figure S23 in the Supporting Information.

The ligand L^{1a} shows a reversible reductive response at -0.89 V along with an irreversible response at -1.34 V. The ligand L^2 , on the other hand, showed two reversible reductive responses at -0.96 and -1.11 V. It is worth mentioning here that these reduction potential values of $L^{1a/b}$ and \widecheck{L}^2 are anodically shifted in comparison to their similar analogues 2,6bis(arylimino)pyridine (L^3) and 2,6-bis(arylazo)pyridine) (L^4), respectively.^{9c,14,15} Complexes 1a,b showed two reductive waves in the potential range -0.2 to -0.8 V. Notably the first reductive response is reversible, while the second response is quasi-irreversible in nature. Complex 2 shows two irreversible reductive waves at -0.21 and -0.81 V. The complex $[3a](ClO_4)_2$ shows a one-electron reversible oxidation at 0.22 V, two reversible one-electron reduction processes at -0.32 and -0.82 V, respectively, and two quasi-reversible reduction processes at -0.93 and -1.350 V, respectively. The oneelectron nature of these processes has been confirmed by comparison of the current height with the redox response of the ferrocene/ferrocenium couple under identical experimental conditions and also by exhaustive electrolyses of $[3a](ClO_4)_2$ at 0.3 V for the reversible oxidation and at -0.4 and -0.9 V, respectively, for the two reversible reductive responses. The complex $[4](ClO_4)_2$ showed a similar one-electron oxidation at 0.15 V and multiple reversible/quasi-reversible reductive waves in the potential range -0.3 to -1.5 V.

To gain insight into the nature of the electronic levels associated with the reversible redox responses, electrochemically generated oxidized and reduced complexes were studied



Figure 8. Zero-field ⁵⁷Fe Mössbauer spectra of (a) 1b (blue circles) and (b) $[3b](ClO_4)_2$ (purple circles) at 80 K. The solid lines represent simulations with Lorentzian doublets.

Table 2. Cyclic Voltammetry Da	ata ^{<i>a,b</i>} of L ^{1a} , L ^{1b} , L	² , 1a, 1b, 2, [3	a](ClO ₄) ₂ , [3	$3b](ClO_4)_2$, and [4](ClO ₄)	1_2
--------------------------------	--	------------------------------	---	----------------	------------------------------	-------

compound	oxidation (V) ($\Delta E_{\rm p}$ (mV))	reduction (V) $(\Delta E_p (mV))$
L^{1a}		-0.89 (110), -1.34
L ^{1b}		-0.87 (100), -1.31
L^2		-0.96 (75), -1.11 (85)
1a		-0.20(71), -0.73(170)
1b		-0.19 (75), $-0.71(170)$
2	0.80	-0.21, -0.81
$[3a](ClO_4)_2$	0.22 (70)	-0.32 (72), -0.82 (75), -0.93, -1.35
$[3b](ClO_4)_2$	0.24 (70)	-0.30 (70), -0.81 (72), -0.90, -1.34
$[4](ClO_4)_4)$	0.15 (72)	-0.33 (68), -0.81 (63), -1.00 (140), -1.17 (74), -1.48 (92)

^{*a*}Conditions: solvent, CH₃CN; supporting electrolyte, Bu₄NClO₄ (0.1 M); reference electrode, saturated Ag/AgCl. ^{*b*}Solute concentration ca. 10⁻³ M. $\Delta E_p = E_{pa} - E_{pc}$; scan rate 50 mV s⁻¹.



Figure 9. Cyclic voltammograms of L^{1a} (black), L^{2} (red), $[3a](ClO_{4})_{2}$ (green), and $[4](ClO_{4})_{2}$ (blue) in CH₃CN.

by EPR spectroscopy at 77 K. The one-electron-reduced ligands $[\mathbf{L}^{1a}]^{-}$ and $[\mathbf{L}^{2}]^{-}$ showed single-line EPR spectra at g = 2.005 and g = 2.004, as expected for ligand-centered radicals of

similar type.⁹ However, no ¹⁴N hyperfine coupling is observed in the EPR spectra under our experimental conditions. The one-electron-reduced complex $[1b]^-$ generated by exhaustive electrolysis at -0.35 V under an argon atmosphere shows a strong-single line EPR signal at g = 1.996 at 77 K. The oneelectron-reduced complexes $[3a]^+$ and $[4]^+$, generated by exhaustive electrolysis at -0.4 V, also showed single-line EPR spectra characteristic of organic radicals (Figure 10). The twoelectron-reduced species 3a and 4 were found to be EPR silent. Attempts were also made to characterize the three- and fourelectron-reduced complexes [4]⁻ and [4]²⁻; however, we could not generate them in a pure state by exhaustive electrolysis. These experimental results are in agreement with DFT calculations, which show that lowest unoccupied molecular orbitals (LUMO, LUMO+1, LUMO+2) of L^{1a}, L^{1b}, L², 1, 2, $[3](ClO_4)_2$, and $[4](ClO_4)_2$ are primarily ligand centered, mainly localized on the azo chromophore with partial delocalization on the phenanthroline moiety. The reductions in these complexes are, therefore, assigned to occur at the ligands rather than at the metal, the oxidation state of the metal remaining invariant. The highest occupied molecular orbitals in $[3](ClO_4)_2$ and $[4](ClO_4)_2$ were, however, found to be mainly localized on the metal. The reversible oxidative waves observed for $[3](ClO_4)_2$ and $[4](ClO_4)_2$ were assigned as metalcentered oxidations.

Electronic Structures and UV–Vis Spectra. The newly synthesized ligands and all of their Fe complexes were thoroughly investigated using density functional theory (DFT) with the B3LYP functional. The optimized structures reproduce the experimental data quite well. Selected calculated bond lengths and angles are compared with the corresponding experimental values in Table 1.



Figure 10. EPR spectra of $[L^{1a}]^{\bullet-}$ (black), $[1b]^{-}$ (green) and $[3a]^{+}$ (blue) after electrochemical reduction of the precursors L^{1a} , 1b, and 3a, respectively.



Figure 12. Spin density plots of 1a (a), $[3a]^{3+}$ (b), and $[3a]^+$ (c).

The ligands L^{1a} and L^{2} along with their one- and twoelectron-reduced analogues $[L^{1a}]^{-}$, $[L^{2}]^{-}$, $[L^{1a}]^{2-}$, and $[L^{2}]^{2-}$ were optimized. Calculated bond lengths of the ligands in three different oxidation states are summarized in Table 1, and the molecular orbital pictures are displayed in Figures S24 and S25 in the Supporting Information. Molecular orbital analysis clearly reveals that the lowest unoccupied MOs of L^{1a} and L² are mainly centered on the azo chromophore(s). The oneelectron-reduced $[L^{1a}]^{\bullet-}$ and $[L^2]^{\bullet-}$ have doublet ground states. In [L^{1a}]^{•-} the net spin density is primarily delocalized over the azo chromophore(s) and phenanthroline ring, whereas in the case of $[L^2]^{\bullet-}$ the net spin density is found to be delocalized over the two azo chromophores. As expected, in $[L^{1a}]^{\bullet-}$ and $[L^2]^{\bullet-}$ the N-N distances were found to be considerably elongated in comparison to those of the neutral L^{1a} and L^2 . The two-electron-reduced ligand $[L^{1a}]^{2-}$ has an S =0 ground state with an N-N distance of 1.379 Å. On the other hand, the two-electron-reduced analogue of L^2 possesses an S =1 ground state having one electron on each azo chromophore with an average N-N distance of 1.356 Å. The corresponding singlet state is 3.03 kcal mol⁻¹ higher in energy. Spin density plots for $[L^{1a}]^{\bullet-}$, $[L^2]^{\bullet-}$, and $[L^2]^{\bullet-2-}$ are shown in Figure 11. The most stable structure of complexes 1a and 2 was found

The most stable structure of complexes 1a and 2 was found to have an S = 2 ground state with the electronic structure description $[Fe^{II}(L^{1a,2})Cl_2]$. High-spin Fe^{II} ($S_{Fe} = 2$) is coordinated to two chlorido ligands and a neutral ligand L^{1a} or L^2 ($S_{L^1/L^2} = 0$) that is bound to the iron center in a tridentate fashion. In accordance with the experimentally observed Mössbauer parameters, the alternative electronic structure possibility, $[Fe^{III}(L^{1,2})^{\bullet-}Cl_2]$, having a high-spin Fe^{III} ($S_{Fe} =$ S/2) center coordinated to two chlorido ligands and a oneelectron-reduced azo anion radical ligand ($L^{1/2}$)^{$\bullet-$} ($S_{L^1/L^2} = 1/2$) showing antiferromagnetic coupling was found to be 3.16 kcalmol⁻¹ higher in energy. The spin density plot of 1a is shown in Figure 12, and that of complex 2 is displayed in Figure S30 in the Supporting Information. The geometries of

the complexes $[3a]^{2+}$ and $[4]^{2+}$ were also well reproduced by DFT studies. Both complexes were found to have closed-shell singlet (S = 0) electronic configurations best described as $[Fe^{II}(L^{1,2})_2]$; all attempts to locate open-shell singlet configurations $[Fe^{III}(L^{1a})^{\bullet-}(L^{1a})]^{2+}$ or $[Fe^{IV}\{(L^{1a})^{\bullet-}\}_2]^{2+}$ using the BS-DFT approach converged back to the closedshell configuration. In $[3a]^{2+}$ and $[4]^{2+}$ a low-spin Fe(II) center is coordinated by two neutral tridentate ligands in a meridional fashion with an average N–N distance of 1.282 Å (for $[3a]^{2+}$) and 1.278 Å (for $[4]^{2+}$), respectively, in good agreement with the Mössbauer spectroscopic analysis. Calculated metrical parameters are collected in Table 1, and MOs are shown in the Supporting Information. Molecular orbital analysis reveals that the high-lying occupied MOs of the complexes 1a, 2, $[3a]^{2+}$, and $[4]^{2+}$ are mainly metal-centered with a small contribution from the ligands, whereas the low-lying unoccupied MOs are ligand-based (Figures S26-S29 in the Supporting Information).

Geometry optimizations were also carried out on the reduced and oxidized forms of complexes $[3a]^{2+}$ and $[4]^{2+}$. Optimized structural parameters for the computed ground states of 3a, $[3a]^+$, $[3a]^{3+}$, 4, $[4]^+$, and $[4]^{3+}$ are collected in Table 1. Both the one-electron-oxidized and -reduced complexes $[3a]^{3+}, [4]^{3+},$ $[3a]^+$, and $[3]^+$ have S = 1/2 ground states. However, spin density analysis shows that the net spin is mainly localized on the Fe center (Figure 12b) in the case of the one-electronoxidized complexes, indicating metal-centered oxidation during the $[3/4]^{2+} \rightarrow [3/4]^{3+}$ conversion, whereas the net spin density was found to be localized mainly on the ligands in the oneelectron-reduced analogues (Figure 12c), pointing to the ligand-centered reduction during $[3,4]^{2+} \rightarrow [3,4]^+$ conversion. These results are in agreement with experiment: viz., EPR data indicating ligand -centered radicals for complexes $[3]^+$ and $[4]^+$. The two-electron-reduced complexes 3a and 4 feature an S = 0ground state, as observed in the EPR studies.

The optical absorption spectra of L^1 , L^2 , 1, and 2 were recorded in dichloromethane, and those of $[3](ClO_4)_2$ and $[4](ClO_4)_2$ were recorded in acetonitrile. The experimental spectral results are summarized in Table 3, and the

Table 3. UV–Vis–NIR Data^a

compound	$\lambda_{ m max}~(m nm)~(arepsilon~(M^{-1}~ m cm^{-1}))$
L^{1a}	249 (15100), 287 (13900, s), 354 (12700)
L^{1b}	241 (14300), 265 (10400, s), 356 (12900)
L^2	311 (40400), 358 (30800, s)
1a	240 (20300), 332 (13200), 402 (14000), 555 (1540, s), 904 (1819, b) (1819)
1b	342 (11050), 403 (12500), 546 (890, s), 911 (720, b)
2	318 (50700), 363 (35200), 924 (2040, b)
$[3a](ClO_4)_2$	234 (20800), 296 (16050, s), 391 (18300), 674 (3500)
$[3b](ClO_4)_2$	304 (16000, s), 392 (16200), 681 (1970)
$[4](ClO_4)_2$	305 (36700), 672 (2000)

^a $L^{1a,b}$, L^2 , 1a,b, and 2 in CH₂Cl₂ and [3a](ClO₄)₂, [3b](ClO₄)₂, and [4](ClO₄)₂ in CH₃CN. Abbreviations: b, broad; s, shoulder.



Figure 13. Electronic spectra of L^{1b} (black), L^2 (blue), **1b** (purple), **2** (olive), [**3b**](ClO₄)₂ (magenta), and [4](ClO₄)₂ (orange) in CH₂Cl₂ and CH₃CN, respectively.

corresponding spectra are shown in Figure 13. The ligands L^1 and L^2 show intraligand $n \rightarrow \pi$ and $\pi \rightarrow \pi^*$ transitions in the region 240–360 nm.⁸ Complexes 1 and 2 show strong absorption peaks in the region 300–400 nm along with broad bands at 911 nm (for 1b) and 924 nm (for 2). These low-energy transitions are assigned as metal to ligand charge transfer transitions (HOMO-1(α) \rightarrow LUMO(α) (31%), HOMO-1(β) \rightarrow LUMO(β) (31%)). Complexes [3]²⁺ and [4]²⁺ show broad absorption maxima at 681 and 672 nm, respectively, along with intraligand charge transfer transitions in the region 300–400 nm.

Catalytic Alcohol Oxidation. We were curious to use our newly synthesized complexes as catalysts to bring about some useful chemical transformations. To start with, we chose the coordinatively unsaturated complexes 1 and 2 for performing catalytic alcohol oxidation reactions.

Initial studies were focused on finding the optimal reaction conditions for the catalytic alcohol oxidation reaction using diphenylmethanol (5i) as the model substrate and complex 1a as the catalyst. Various reaction conditions, including bases, solvents, and reaction temperatures, were screened. The reaction proceeded most efficiently in solvents such as heptane and toluene, whereas reactions in more polar and potentially coordinating solvents such as MeCN, dioxane, methanol, and DMF afforded poor yields. Among the series of bases tested only alkali-metal *tert*-butoxides ($MO^{t}Bu$, M = Li, Na, K) were found to be effective (Table 4, entries 8-11); with other bases such as K₃PO₄, K₂CO₃, Cs₂CO₃, and NaOH, only a trace amount of alcohol oxidation was observed. The best result was obtained with 10 mol % KO^tBu as base. The highest conversion of diphenylmethanol (5i) to benzophenone (5ii) was achieved when the reaction was carried out at 75 °C in toluene for 5 h in the presence of 10 mol % KO^tBu and 3.0 mol % of the catalyst (Table 4, entry 11). Lowering the temperature or catalyst loading below 3.0 mol % leads to poor conversion of the alcohols to the corresponding aldehydes or ketones.

Among the newly synthesized iron complexes, complex 1b having an electron-withdrawing Cl group at the para position of the phenyl ring was found to be more effective than 1a (Table 4, entry 17). Complex 2 was found to be equally efficient; however, because of its comparatively lower solubility, catalytic reactions require longer times.

It is worth mentioning here that upon addition of KO^tBu to a solution of the catalyst $[FeL^{1a/b}Cl_2]$ (1a,b) the initial brown color of the solution instantaneously changes to reddish brown, as observed during exhaustive electrolysis at -0.35 V. Moreover, upon addition of KO^tBu to a solution of the free ligand L^{1a,b} the initial orange color of the solution immediately changes to dark orange, as observed during electrochemical reduction of the free ligand. The alkali-metal tert-butoxides are known to act as reducing agents; there are some reports showing that $MO^{t}Bu$ (M = Li, Na, K) reduces 1,10phenanthroline to generate the corresponding one-electronreduced 1,10-phenanthroline anion radical.¹⁶ These experimental observations in our case indeed point to the possibility of KO^tBu-mediated reduction of 1b to $[1b]^-$ and the involvement of the one-electron-reduced complex $[1b]^-$ in the catalytic cycle (cf. below), as recently reported by Goswami and co-workers for a related system.¹¹ Formation of only a trace amount of benzophenone (5ii) in the presence of other nonreducing bases such as K₃PO₄, K₂CO₃, Cs₂CO₃, and NaOH further indicates the possibility of the involvement of the oneelectron-reduced complex $[1b]^-$ during catalytic turnover.

To confirm the possibility of KO^tBu-mediated reduction of 1b as well as L¹, leading to the formation of ligand-centered radicals, EPR experiments were carried out separately with solutions containing 1:1 mixtures of KO^tBu and catalyst 1b and free ligand L1a, respectively (Figures S34 and S38 in the Supporting Information). Indeed, both reaction mixtures gave single-line EPR spectra with g = 1.997 and g = 2.004 (Figures \$34 and \$38), respectively, as was observed before for the oneelectron-reduced complexes $[1b]^-$ and $[L^{1a}]^{\bullet-}$ (Figure 10 and Figures S34 and S38).¹⁷ These experimental data are in agreement with the EPR spectra reported by Lei and coworkers during KO^tBu-mediated reduction of free 1,10-phenanthroline.^{16a} Since KO^tBu is a weak reducing agent, EPR experiments were carried out to quantify the extent of reduction. Spin quantification measurements using TEMPO as the standard showed that, in dichloromethane solvent, addition of 1.0 equiv of KO^tBu to 1b leads to 63% conversion of 1b to $[1b]^{-}$ in 5 h and at 75 °C; using toluene as the solvent, 72% of **1b** is converted to $[1b]^-$ in 3 h. However, in case of the free

Table 4. Optimization of Reaction Conditions $^{a-d}$

 $\cap \vdash$

	Ì	Í 🌱 🎽 🧎	Fe-catalyst, Base			
	, i i i i i i i i i i i i i i i i i i i	5i 5i	Solvent, Temp (C)	5ii 5ii		
entry	catalyst (amt (mol %))	temp (°C)	solvent	base (amt)	time (h)	yield (%)
1	1a (10)	120	toluene	K ₃ PO ₄ (10 mol %)	12	10
2	1a (10)	120	toluene	K ₂ CO ₃ (10 mol %)	12	5
3	la (10)	120	toluene	Cs ₂ CO ₃ (10 mol %)	12	trace
4	1a (10)	120	toluene	NaHCO ₃ (10 mol %)	12	trace
5	1a (10)	120	toluene	NaOMe (10 mol %)	12	trace
6	la (10)	120	toluene	NEt ₃ (10 mol %)	12	10
7	la (10)	120	toluene	NaOH (10 mol %)	12	trace
8	la (10)	75	toluene	Li ^t BuO (10 mol %)	12	72
9	1a (10)	75	toluene	Na ^t BuO (10 mol %)	12	81
10	1a (10)	75	Toluene	K ^t BuO (10 mol %)	12	88
11	1a (3.0)	75	toluene	K ^t BuO (10 mol %)	5	88
12	1a (10)	75	DMF	K ^t BuO (10 mol %)	12	trace
13	la (10)	75	EtOH	K ^t BuO (10 mol %)	12	5
14	la (10)	75	CH ₃ CN	K ^t BuO (10 mol %)	12	<10
15	1a (10)	75	THF	K ^t BuO (10 mol %)	12	80
16	1a (10)	75	heptane	K ^t BuO (10 mol %)	12	78
17	1b (3.0)	75	toluene	K ^t BuO (10 mol %)	5	92
18	1b (3.0)	60	toluene	K ^t BuO (10 mol %)	5	60
19	2 (3.0)	75	toluene	K ^t BuO (10 mol %)	5	68
20	[1b] ⁻ (2.0)	75	toluene		24	trace
21	[1b] ⁻ (2.0)	75	toluene	K ^t BuO (5.0 mol %)	4	95
22	[1b] ⁻ (2.0)	75	toluene	NaOH (5.0 mol %)	4	95
23	[1b] ⁻ (2.0)	75	toluene	NaOMe (10 mol %)	4	61
24	[1b] ⁻ (2.0)	75	toluene	K ₂ CO ₃ (10 mol %)	4	61
25	[1b] ⁻ (2.0)	75	toluene	Cs ₂ CO ₃ (10 mol %)	4	48
26	[1b] ⁻ (2.0)	75	toluene	K ₃ PO ₄ (10 mol %)	4	49
27		75	toluene	K ^t BuO (10 mol %)	12	<5
28		room temp	toluene	K ^t BuO (2.0 equiv)	12	45
29	$FeCl_2$ (3.0)	75	toluene	K ^t BuO (10 mol %)	5	<5
30	$\operatorname{FeCl}_3(3.0)$	75	toluene	K ^t BuO (10 mol %)	5	<5
31	L/L^{1} (3.0)	75	toluene	K ^t BuO (10 mol %)	5	<5
32 ^d	$1b/[1b]^{-}(3.0)$	75	toluene	K ^t BuO (10 mol %)	3	<5

^aAlcohol (1.0 mmol). ${}^{b}[1b]^{-}$ was obtained via quantitative reduction of 1b by cobaltocene. ^cIsolated yields after column chromatography. ^dTEMPO was used as radical scavenger.

ligand, only 49% conversion of $[L^{1a}]$ to $[L^{1a}]^{\bullet-}$ was observed in 5 h. To further confirm the KO^tBu-mediated reduction of 1b and L^{1b}, the reactions between KO^tBu with 1b and L^{1b} were monitored separately using UV-vis spectroscopy(see Figures S34, S38, and S39 in the Supporting Information). Upon addition of 1.0 equiv of KO^tBu to a solution of 1b, the absorption peaks at 348 and 283 nm increase and the intensity of the broad peak at 911 nm decreases, as was observed during quantitative one-electron reduction of 1b by cobaltocene.

After having evidenced the involvement of the one-electronreduced complex $[1b]^-$ as the active catalyst during catalytic alcohol oxidation reactions, we decided to reoptimize the catalytic reaction using the preformed $[1b]^-$ as the catalyst and diphenylmethanol (5i) as the model substrate in toluene (Table 4, entries 20–26). Pleasingly, using preformed $[1b]^-$ as the catalyst, the reaction proceeded even with bases such as K₃PO₄, K₂CO₃, Cs₂CO₃, and NaOH, with which only a trace amount of benzophenone was obtained as the dehydrogenated product when parent 1b was used as the catalyst (Table 4, entries 22-26). Reactions proceeded even with 1.0 mol % of base loading. The highest conversion of diphenylmethanol (5i)

to benzophenone (5ii) was obtained when the reaction was carried out at 75 °C in toluene for 4 h in the presence of 5 mol % KO^tBu or NaOH, and only 2.0 mol % of [1b]⁻ is sufficient (Table 4, entries 21 and 22). However, the reaction did not occur in absence of base. These experimental results indeed support the involvement of the one-electron-reduced complex $[1b]^{-}$ as the active catalyst during catalytic alcohol oxidation reactions. Therefore, the catalytic oxidation of benzyl alcohols can be achieved either using a combination of $[1b]^{-}$ (2.0 mol %) and NaOH or KO^tBu (5.0 mol %) or, alternatively, 1b (3.0 mol %) and 10 mol % of KO^tBu, which other than acting as a base also acts as a reducing agent^{16a} to form the active catalyst $[1b]^-$ in situ from 1b.

Control experiments showed that no product was obtained in the absence of catalyst 1b; only a trace amount of product was obtained in the presence of only ligand and base (10 mol % KO^tBu). Other iron sources such as FeCl₂ and FeCl₃ were also found to be unable to convert alcohols to the corresponding carbonyls under the optimized reaction conditions. Only a trace amount (<5%) of carbonyl compounds were formed in the presence of 10 mol % KO^tBu at 75 °C. In the presence of a

Table 5. Substrate Scope^{a-c}



^{*a*}Conditions: complex **1b** (0.03 mmol), alcohol (1.0 mmol), KO^tBu (10.0 mol %), reaction time 5 h. ^{*b*}Conditions: complex **1b** (0.02 mmol), cobaltocene (0.02 mmol), alcohol (1.0 mmol), NaOH (5.0 mol %), reaction time 4 h. ^{*c*}Isolated yields after column chromatography. ^{*d*}The yield in parentheses was obtained when preformed $[1b]^-$ was used as the catalyst.

basic environment alcohols are highly susceptible to aerobic oxidation even in the absence of any catalyst.¹⁷ Therefore, the amount of base used during catalytic reactions should be as low as possible. To assess the background reactivity, the catalytic alcohol oxidation was studied with different amounts of base loading. Interestingly, use of excess KO^tBu (2.0 equiv) leads to almost 45% conversion of the alcohols to the corresponding carbonyls at room temperature even in the absence of any Fe catalyst (Table 4, entry 28). However, only trace amounts (<5%) of carbonyl compounds were formed in the presence of 10 mol % KO^tBu even at 75 °C.

Catalytic oxidation of various substituted benzyl alcohols with different electronic properties and functional groups were studied to explore the substrate scope and versatility of the developed catalytic methodology. Almost similar conversion of alcohols to the corresponding aldehydes or ketones were obtained using either the preformed one-electron-reduced complex $[1b]^-$ (2.0 mol %) and NaOH (5.0 mol %) as the base or a combination of 1b (3.0 mol %) and 10 mol % KO'Bu. The results are summarized in Table 5. Excellent yields were obtained with alcohols having electron-donating substituents. The presence of electron-donating groups at the ortho, para, or meta position of the benzyl alcohol produces the corresponding aldehyde in high yield. Reactions also proceeded with electron-

withdrawing groups at the para position of benzyl alcohols, albeit leading to lower yields. For example, 4-chlorobenzaldehyde was obtained in 85% yield from the corresponding 4chlorobenzyl alcohol (Table 5, entry 2). However, poor conversion to the aldehyde was obtained in the presence of strongly electron withdrawing groups at the para position of benzyl alcohol. 4-Nitrobenzaldehyde was obtained in only 45% yield from the corresponding 4-nitrobenzyl alcohol (Table 5, entry 3).

Secondary alcohols were also found to be suitable substrates for oxidation to the corresponding ketones. Diphenylmethanol or 1-phenylethanol produced benzophenone and acetophenone in high yields under the same optimized reaction conditions (Table 5, entries 9 and 10). Reactions proceeded with both electron-donating and -withdrawing groups at the phenyl ring of 1-phenylethanol. However, lower yields of the corresponding acetophenone were obtained in the presence of electronwithdrawing groups (Table 5, entries 11-13). Anthracene-9carbaldehyde was also isolated in high yields from the corresponding alcohol (Table 5, entry 7). Heterocyclic alcohols also produce the corresponding aldehydes in high yield. For example, 2-thiophenemethanol produced thiophene-2-aldehyde in 65% yield under the same optimized conditions (Table 5, entry 15). No reaction was observed with *n*-pentanol. To explore the reaction mechanism, a few control experiments were carried out. Kinetic studies of the catalytic reaction using 1-phenylethanol as the substrate showed linear dependence of the rate $k_{\rm obs}$ on both substrate and catalyst concentration (Figures S35 and S36 in the Supporting Information). The rate of the catalytic oxidation of 1-phenylethanol was found to rise linearly when the catalyst loading was varied in the range 1.0–1.75 mol % with respect to the alcohol. Similarly, a linear increase in the rate was observed when the substrate concentration was varied over a range of 5–20 equiv of alcohol with respect to the catalyst.

The coordinated azo ligand is redox active and produces an azo anion radical upon reduction;⁸⁻¹¹ therefore, to check the involvement of ligand-centered redox as well as to confirm the formation of any organic radicals during catalytic turnover, the catalytic reaction was performed in the presence of a radical inhibitor. When an equivalent amount of TEMPO was added to the reaction system, the yield of the reaction decreased drastically (Table 4, entry 32). To gain more information about the involvement of the coordinated azo-aromatic ligand during catalytic turnover, stoichiometric reactions were performed using 1b, 1-phenylethanol (5j), and 10 mol % KO^tBu in toluene under an argon atmosphere. Characterization of the reaction mixture using IR spectroscopy under an argon atmosphere shows N-H stretching at 3025 and 3060 cm⁻¹, as reported by others (Figure S40 in the Supporting Information).^{11,18d} To further confirm the azo to hydrazo conversion during catalytic turnover, the stoichiometric reaction was repeated with deuterated 1-phenylethanol (5j- D_2) under an argon atmosphere. Upon IR spectroscopic analysis of this reaction, new bands at 2310 and 2375 cm⁻ characteristic of N-D stretching were observed. These experimental findings indeed point to the involvement of the coordinated azo-aromatic ligand during catalysis. Similar N-H and N-D stretching frequencies were also observed when the stoichiometric reactions were carried out using 1-phenylethanol (5j), preformed $[1b]^-$, and 5.0 mol % NaOH.

To check the possibility of H₂ evolution during catalytic alcohol oxidation reactions intermolecular hydrogen transfer experiments were carried out in the presence of easily reducible substrates such as 4-methoxybenzaldehyde (5dd) and 2,4dimethoxybenzaldehyde (5ff), respectively, in a closed system.¹² The dehydrogenation of diphenylmethanol (5i) when it is carried out separately in the presence of 5dd and 5ff in a closed system under both inert and aerobic conditions does not produce any hydrogenated product of the aldehydes (5dd or 5ff). Moreover, the formation of H_2O_2 was identified spectrophotometrically under aerobic conditions.¹¹ Finally, to distinguish between the one-electron (HAT) and two-electron (hydride transfer) processes, catalytic oxidation of cyclobutanol was carried out using 1b as the catalyst.^{12i,j} Investigation of the ¹H NMR spectrum of the reaction mixture containing the oxidation products of cyclobutanol indicates the formation of multiple products, including 4-hydroxybutanal as the ringopening product (Figure \$53 in the Supporting Information). These experimental data indeed point to the one-electron (HAT) oxidation pathway and the possibility of hydride atom transfer seems less likely.

Combining all available evidence, we depict a plausible mechanism for the present iron-catalyzed alcohol oxidation reactions in Figure 14. On the basis of the above experimental results along with available literature, the catalytic alcohol oxidation reactions are believed to be catalyzed by the one-



Figure 14. Plausible mechanism for the alcohol oxidation catalyzed by $[Fe(L^{1,2})Cl_2]$.

electron-reduced complex [1b]⁻. The reaction proceeds via the coordination of the deprotonated alcohol to the active catalyst $([1b]^{-})$ to form the intermediate **B**; the base may assist in this step by formally trapping HCl. This is followed by hydrogen atom abstraction from the α -carbon of the coordinated alcohol, leading to an O-coordinated ketyl radical anion (C). In the next step the intermediate C undergoes rapid one-electron oxidation to afford the desired carbonyl compound.^{11,18} During oxidation of the O-coordinated ketyl radical anion both intramolecular metal- and ligand-centered reductions are possible.¹⁸ Involvement of dioxygen has also been proposed in some cases.¹¹ In our case, formation of benzophenone from the stoichiometric reaction of catalyst [1b]⁻ and diphenylmethanol (5i) in the presence of 5.0 mol % NaOH under an argon atmosphere indeed points toward the intramolecular reduction of $[1b]^-$ as proposed by others.^{11,18} However, it is difficult to comment conclusively whether the metal- or the ligand-centered reduction process is involved during the oxidation of the Ocoordinated ketyl radical anion. Intramolecular ligand-centered reduction would generate a phenanthroline anion radical, which is expected to be unstable under oxidative conditions. Therefore, intramolecular ligand-centered reduction (generation phenanthroline radical) seems less likely and we propose metal-centered reduction from Fe(II) to Fe(I) during the oxidation of the O-coordinated ketyl radical anion. In the subsequent steps, the intermediate D, thus formed, abstracts a proton form the alcohol substrate to form intermediate E,¹¹ which in the presence of dioxygen produces H_2O_2 with the regeneration of the azo chromophore.²⁰ Intramolecular electron transfer from an electron-rich Fe(I) center to the reducible azo chromophore then generates B.⁵

CONCLUSIONS

In conclusion, we have reported the two new redoxnoninnocent azo-aromatic pincers L^1 and L^2 and synthesized their Fe complexes with the aim of developing new azoaromatic ligand based catalysts to bring about useful chemical transformations. The ligand L^1 is tridentate, having one easily reducible azo chromophore, whereas L^2 is a tetradentate ligand having two easily reducible azo functions. The coordination behavior of the newly synthesized ligands along with the electronic structures of all the synthesized Fe complexes were studied thoroughly using different spectroscopic tools coupled with DFT computations. Interestingly, the tetradentate ligand L² shows tridentate binding with uncoordinated pendant azo chromophores in complexes 2 and $[4](ClO_4)_2$. The newly synthesized Fe complexes 1 and 2 were successfully used as catalysts for the aerobic oxidation of primary and secondary benzylic alcohols. Mechanistic investigations show that the oneelectron-reduced complexes $[1]^-$ and $[2]^-$ actually act as the active catalysts during these catalytic alcohol oxidation reactions. Moreover, the involvement of the coordinated redox-noninnocent azo-aromatic ligand has also been evidenced. Overall, the ligands L^1 and L^2 open up the possibility of using these azo-aromatic scaffolds in catalysis in combination with suitable metal ions. Our initial results in cross-coupling reactions using 1 and 2 as catalysts are promising, and these findings will be reported in due course.

EXPERIMENTAL SECTION

Materials. $\operatorname{FeCl}_{22} \operatorname{Fe}(\operatorname{ClO}_4)_{22}$ and all alcohols were purchased from Sigma-Aldrich. All other reagents and chemicals were purchased from commercial sources and used without further purifications. Tetrabutylammonium perchlorate was prepared and recrystallized as reported before.¹⁹ *Caution! Perchlorates have to be handled with care with appropriate safety precautions.*

Physical Measurements. UV-vis spectra were recorded with a Jasco spectrometer. ¹H NMR spectra were recorded on Bruker Avance 300/400/500 MHz and JEOL 400 MHz spectrometers, and SiMe₄ was used as the internal standard. A PerkinElmer 240C elemental analyzer was used to collect microanalytical data (C, H, N). ESI mass spectra were recorded on a Micromass Q-TOF mass spectrometer (serial no. YA 263). All electrochemical measurements were performed using a PC-controlled AUT.MAC204 electrochemistry system. Cyclic voltammetry experiments were performed under a nitrogen atmosphere using a Ag/AgCl reference electrode, with a Pt-disk working electrode and a Pt-wire auxiliary electrode, in acetonitrile or dichloromethane containing supporting electrolyte, 0.1 M $[Et_4N]ClO_4$ or 0.1 M [Bu₄N]ClO₄, respectively. A Pt-wire-gauge working electrode was used for exhaustive electrolyses. Room-temperature magnetic moment measurements for 1 and 2 were carried out with a Gouy balance (Sherwood Scientific, Cambridge, U.K.). Temperature-dependent magnetic susceptibility measurements were carried out with a Quantum-Design MPMS-XL-5 SQUID magnetometer equipped with a 5 T magnet in the range from 295 to 2.0 K at a magnetic field of 0.5 T. Mössbauer spectra were recorded with a ⁵⁷Co source in a Rh matrix using an alternating constant acceleration Wissel Mössbauer spectrometer operated in the transmission mode and equipped with a Janis closed-cycle helium cryostat. Isomer shifts are given relative to iron metal at ambient temperature. EPR spectra in the X band were recorded with a JEOL JES-FA200 spectrometer.

Synthesis. Synthesis of L^{1a} . 2-(Phenylazo)-1,10-phenanthroline (L^{1a}) was synthesized via diazotization of 2-amino-1,10-phenanthroline with nitrosobenzene under highly alkaline conditions. The crude reaction mixture was evaporated, and the product was dissolved in dichloromethane and purified by column chromatography using dichloromethane as eluent. Yield: 72%. UV/vis: λ_{max} , nm (ε , M⁻¹ cm⁻¹) 249 (15130), 287 (13915, s), 354 (12735), IR (KBr, cm⁻¹):

1609 (ν , C=N), 1455 (ν , N=N). Anal. Calcd for C₁₈H₁₂N₄: C, 76.04; H, 4.25; N, 19.71. Found: C, 76.09; H, 4.31; N, 19.75. ESI-MS: m/z 285 [L^{1a} + H]⁺. ¹H NMR (400 MHz, CDCl₃): δ 9.27 (s, 1H), 8.44 (d, J = 8 Hz, 1H), 8.31 (d, J = 12 Hz, 1H), 8.18 (s, 3H), 7.89 (s, 2H), 7.69 (s, 1H), 7.56 (s, 3H). ¹³C NMR (400 MHz, CDCl₃): δ 161.61, 152.24, 150.33, 145.97, 145.26, 138.41, 136.05, 132.32, 129.36, 127.61, 125.87, 123.86, 123.19, 113.51, 77.71.

Synthesis of L^{1b} . The ligand L^{1b} was synthesized following the same procedure as described for L^{1a} . Its yield and characterization data are as follows. Yield: 75%. UV/vis: λ_{max} nm (ϵ , M^{-1} cm⁻¹) 241 (14285), 265 (10370, s), 356 (12885). ESI-MS: m/z 319 [L^{1b} + H]⁺. ¹H NMR (400 MHz, CDCl₃): δ 9.27 (s, 1H), 8.42 (d, J = 8 Hz,1H), 8.30 (d, J = 12 Hz, 1H), 8.15 (d, J = 6 Hz, 3H), 7.87 (s, 2H) 7.70 (t, J = 6 Hz, 1H), 7.56(d, J = 12 Hz, 2H).

Synthesis of L². 2,9-Bis(phenyldiazo)-1,10-phenanthroline (L²) was synthesized via the diazotization of 2,9-diaminophenanthroline with nitrosobenzene in highly alkaline medium for 48 h. The crude reaction mixture was evaporated, and the solid was dissolved in dichloromethane and purified by column chromatography using dichloromethane as eluent. Yield: 60%. UV/vis: λ_{max} nm (ε , M⁻¹ cm⁻¹) 311 (40400), 358 (30760, s). IR (KBr, cm⁻¹): 1570 (ν , C=N), 1450 (ν , N=N). Anal. Calcd for C₂₄H₁₆N₆: C 74.21; H 4.15; N, 21.64. Found: C, 74.25; H, 4.21; N, 21.69. ESI-MS: m/z 389 [L² – H]⁺. ¹H NMR (400 MHz, CDCl₃): δ 8.50 (d, J = 12, 2H), 8.23 (d, J = 12, 6H), 7.98 (s, 2H), 7.57 (d, J = 4, 6H). ¹³C NMR (400 MHz, CDCl₃): δ 162.09, 152.52, 145.80, 138.86, 132.51, 129.28, 127.51, 124.07, 114.07, 77.46.

Synthesis of [FeL^{1a}Cl₂] (1a). A 50 mg portion (0.17 mmol) of the ligand L^{1a} was dissolved in ethanol, and 41.3 mg (0.17 mmol) of FeCl₂·6H₂O was added to it. Upon addition of the metal salt the color of the solution immediately changed from orange to brown, which gradually intensified with time. The reaction mixture was refluxed for 5 h in a heating mantle. A dark precipitate was formed, which was collected by filtration of the reaction mixture. The complex [Fe(L^{1a})Cl₂] was purified by fractional crystallization using a dichloromethane—hexane solvent mixture. Its yield and characterization data are as follows: Yield: 90%. UV/vis: λ_{max} nm (ε , M⁻¹ cm⁻¹) 240 (20260), 332 (13170), 402 (14040), 555 (1540, s), 904 (1820, b), IR (KBr, cm⁻¹): 1650 (ν C=N), 1415 (ν (N=N)), Anal. Calcd for C₁₈H₁₂Cl₂FeN₄: C, 52.59; H, 2.94; N, 13.63. Found: C, 52.65; H, 3.03; N, 13.64. ESI-MS: m/z 408 [1a – H]⁺.

Synthesis of $[FeL^{1b}Cl_2]$ (1b). This was synthesized following the same procedure as described for 1a. Its yield and characterization data are as follows: Yield: 92%. UV/vis: λ_{max} nm (ε , M⁻¹ cm⁻¹) 342 (11050), 403 (12510), 546 (885, s), 911 (720, b). IR (KBr, cm⁻¹): 1600 (ν (C=N)), 1410 (ν (N=N)), Anal. Calcd for C₁₈H₁₁Cl₃FeN₄: C, 48.53; H, 2.49; N, 12.58. Found: C, 48.47; H, 2.60; N, 12.64.

Synthesis of $[FeL^2Cl_2]$ (2). A 50 mg portion (0.12 mmol) of the ligand L^{2a} was dissolved in ethanol, and 30.2 mg (0.12 mmol) FeCl₂. 6H₂O was added to it. Upon addition of the metal salt the color of the solution immediately changed from orange to brown, which gradually intensified with time. The reaction mixture was refluxed for 5 h in a heating mantle. A dark precipitate was formed, which was collected by filtration of the reaction mixture. The complex $[Fe(L^2)Cl_2]$ was purified by fractional crystallization using a dichloromethane—hexane solvent mixture. Its yield and characterization data are as follows: Yield: 90%. UV/vis: λ_{max} , nm (ε , M^{-1} cm⁻¹) 318 (50670), 363 (35165), 924 (2045, b), IR (KBr, cm⁻¹): 1600 (ν (C=N))), 1435 (ν (N=N)). Anal. Calcd for $C_{24}H_{16}Cl_2FeN_6$: C, 55.95; H, 3.13; N, 16.31. Found: C, 55.90; H, 3.23; N, 16.37. ESI-MS, *m/z* 514 [2 – H]⁺.

Synthesis of $[Fe(L^{1a})_2](ClO_4)_2$ ([3a](ClO₄)₂). A 50 mg portion (0.17 mmol) of the ligand L^{1a} was dissolved in ethanol, and 20.7 mg (0.08 mmol) Fe(ClO₄)₂ was added to it. Upon addition of the metal salt the color of the solution immediately changed from orange to green. The reaction mixture was stirred for 5 h. A green precipitate was formed, which was collected by filtration of the reaction mixture. The complex [Fe(L^{1a})₂]ClO₄ was purified by fractional crystallization using an acetonitrile–toluene solvent mixture. Its yield and characterization data are as follows. Yield: 90%, ESI-MS: m/z 452 [2]⁺. UV/vis: λ_{max} nm (ε , M⁻¹ cm⁻¹) 234 (20835), 296 (16050, s), 391 (18320), 674 (3510), IR (KBr, cm⁻¹): 1635 (ν (C=N)), 1415 (ν (N=N)), Anal.

Table 6. Crystal Data an	ld Structure Refinement Par	ameters of L^{1a} (ClO ₄), 1b, 2	, [3b](ClO ₄) ₂ , and [4](ClO	4)2	
	L^{1a} ·ClO ₄ ·H ₂ O	lb	2	$[3b](CIO_4)_2$	$[4](CIO_4)_2$
empirical formula	$C_{18}H_{13}N_4\cdot ClO_4\cdot H_2O$	$C_{18}H_{11}Cl_3FeN_4$	$C_{24}H_{16}CIFeN_{6}CI$	$2(C_{36}H_{22}Cl_2FeN_8)\cdot 4(ClO_4), H_2O$	$2(C_{48}H_{32}FeN_{12})\cdot 4(ClO_4)\cdot CH_2Cl_2$
formula wt	402.79	445.51	515.18	1802.55	2148.14
temp (K)	150	150	150	150	150
cryst syst	monoclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\overline{1}$	$P\overline{1}$	$P\overline{I}$	$P2_1/c$
a (Å)	6.9758(5)	8.8693(3)	9.1100(4)	12.8260(8)	18.6810(11)
b (Å)	19.0594(12)	9.8094(3)	9.1235(4)	13.8761(9)	12.1078(7)
c (Å)	13.4429(9)	10.5901(3)	14.2715(6)	20.6731(13)	21.0116(11)
α (deg)	06	90.907(1)	79.994(2)	83.825(3)	90
β (deg)	98.582(4)	91.815(1)	76.277(2)	81.290(3)	91.357(2)
γ (deg)	06	109.154(1)	68.620(2)	81.225(3)	90
V (Å ³)	1767.3(2)	869.59(5)	1068.01(8)	3580.8(4)	4751.2(5)
Z	4	2	2	2	2
$D_c (Mg m^{-3})$	1.514	1.702	1.602	1.672	1.502
cryst dimens (mm)	$0.04 \times 0.20 \times 0.40$	$0.04 \times 0.20 \times 0.28$	$0.02 \times 0.14 \times 0.16$	$0.10 \times 0.18 \times 0.20$	$0.04 \times 0.20 \times 0.30$
$\mu (\mathrm{mm}^{-1})$	0.257	1.338	0.983	0.789	0.555
F(000)	832	448	524	1828	2196
θ min, max (deg)	1.9, 27.1	1.9, 28.0	2.4, 27.2	1.5, 25.5	1.9, 27.2
no. of rflns collected	19412	20859	25959	13166	30289
no. of unique rflns	3888	4179	4703	13166	10526
goodness of fit on F^2	1.02	1.05	1.06	1.15	1.03
final R indices $(I > 2\sigma(I))$	R1 = 0.0531, w $R2 = 0.1567$	R1 = 0.0213, WR2 = 0.0590	R1 = 0.0384, w $R2 = 0.0956$	R1 = 0.0610, WR2 = 0.1496	R1 = 0.0718, wR2 = 0.2401
largest diff. peak and hole	-0.54/0.74	-0.22/0.38	-0.37/1.41	-0.71/0.71	-0.58/1.19

Calcd for $C_{36}H_{24}Cl_2FeN_8O_8$: C, 52.51; H, 2.94; N, 13.61. Found: C, 52.56; H, 3.01; N, 13.63. ESI-MS: m/z 624 [3a]⁺.

Synthesis of $[Fe(L^{1b})_2](ClO_4)_2$ ([**3b**]($ClO_4)_2$). This was synthesized following the same procedure as described for $[3a](ClO_4)_2$. Its yield and characterization data are as follows. Yield: 90%. UV/vis: λ_{max} , nm (ε , M^{-1} cm⁻¹) 304 (16000, s), 392 (16245), 681 (1965). ESI-MS, m/z 693 $[3b - H]^+$. ¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, J = 12 Hz, 1H), 7.50 (d, J = 8 Hz, 1H), 6.73 (d, J = 12 Hz, 1H), 6.52 (m, 2H), 5.58 (t, J = 8 Hz, 1H), 5.26 (s, 1H), 5.10 (m, 2H), 4.36 (d, J = 8 Hz, 2H). ¹³C NMR (400 MHz, CDCl₃): δ 195.90, 186.22, 178.48, 170.64, 168.84, 167.12, 162.71, 156.55, 40.13.

Synthesis of $[Fe(L^2)_2](ClO_4)_2$ [4](ClO₄)₂. A 50 mg portion (0.12 mmol) of the ligand was dissolved in ethanol, and 16.3 mg (0.064 mmol) of the metal salt $Fe(ClO_4)_2$ was added to it. The color of the solution immediately changed from orange to green after addition of the metal salt. The color of the solution gradually intensified. The solution was refluxed for 5 h. The solvent was evaporated under low pressure. The resulting solid was dissolved in DCM and recrystallized from a DCM–hexane mixture. Its yield and characterization data are as follows. Yield: 80%. UV/vis: λ_{max} nm (ε , M⁻¹ cm⁻¹) 305 (36655), 672 (2010), IR (KBr, cm⁻¹): 1595 (ν (C=N)), 1435 (ν (N=N)). Anal. Calcd for C₄₈H₃₂Cl₂FeN₁₂O₈: C, 55.89; H, 3.13; N, 16.29.Found: C, 55.92; H, 3.17; N, 16.33. ESI-MS, *m*/*z* 832 [4]⁺. ¹H NMR (400 MHz, CDCl₃): δ 7.97 (m, 1H), 7.80 (m, 1H), 7.55 (m, 5H), 7.44 (m, 2H), 6.80 (t, *J* = 10 Hz, 1H), 6.36 (m, 14H), 5.90 (m, 2H), 5.15 (m, 4H), 4.93 (m, 2H).

Catalytic Alcohol Oxidation Using 1b as the Catalyst. Under aerobic conditions, 1b (3.0 mol %) and the respective alcohols (1.0 mmol) were placed in a 50 mL round-bottom flask. Subsequently KO'Bu (0.1 mmol, 10 mol %) and 3 mL of dry toluene were added. The reaction mixture was stirred for 5.0 h at 75 °C. After the reaction was complete, the resulting mixture was evaporated to dryness using a rotary vacuum evaporator and extracted with hexane. The volume of the hexane solution was reduced and purified by column chromatography to get the products. The pure products were identified by ¹H NMR.

Catalytic Alcohol Oxidation Using Preformed $[1b]^-$ as the Catalyst. Under an argon atmosphere 8.9 mg (2.0 mol %) of 1b was placed in a oven-dried Schlenk tube. A 5.0 mL portion of dry and degassed toluene was added to it with stirring. To this suspension was added 3.8 mg (1.0 equiv) of cobaltocene, and the mixture was stirred for 10 min under an inert atmosphere. The color of the solution changed from dark brown to reddish brown. To this solution were added 1.0 mmol of the respective alcohol and 2.0 mg of NaOH. The Schlenk tube was then placed in an oil bath preheated at 75 °C, and the reaction was continued for 4.0 h in air.

Detection of Hydrogen Peroxide during the Catalytic Reactions..^{11,20} The formation of H_2O_2 during catalytic alcohol oxidation reactions was detected spectrophotometrically following the gradual development of the characteristic absorption band for I_3^- at 350 nm. The catalytic oxidation of diphenylmethanol (5i) was carried out in a round-bottom flask containing 1.0 mmol of the substrate 5i, 0.3 mmol of catalyst 1b, and 0.1 mmol of KO^tBu in 10 mL of dry toluene. The reaction mixture was heated at 75 °C for 4 h. A 10 mL portion of water was added to the reaction mixture, and the whole solution was extracted three times with dichloromethane. The separated aqueous layer was then acidified with H2SO4 to pH 2 to stop further oxidation. To it were added 1.0 mL of a 10% solution of KI and a few drops of a 3% solution of ammonium molybdate. Hydrogen peroxide oxidizes I⁻ to I₂, which reacts with excess I⁻ to form I_3^- according to the following chemical reactions: (i) $H_2O_2 + 2I^ + 2H^+ \rightarrow 2H_2O + I_2$; (ii) $I_2(aq) + I^- \rightarrow I_3^-$. The reaction rate was slow and increased with increasing concentrations of acid.

Control Experiment for Detection of N–H/N–D Stretching.¹¹ Under an argon atmosphere, 1.0 mmol of diphenylmethanol (**Si**), 1.0 mmol of catalyst **1b**, and 0.1 mmol of K^tBuO were placed in a flame-dried Schlenk tube. The tube was capped with a Teflon screw cap, evacuated, and back-filled with argon. The screw cap was replaced with a rubber septum. Then, 5 mL of dry and deoxygenated toluene was added. The solution was stirred for 8.0 h at 75 °C. The solution was filtered; the solvent was evaporated under vacuum. The IR spectrum of the resultant reaction mixture showed characteristic stretching due to N–H bonds: ν (N–H) 3025 and 3060 cm⁻¹.

A similar experiment was also performed with deuterated diphenylmethanol (Ph₂CDOD) (**5i-D**₂) following the same experimental procedure as mentioned above. The IR spectrum of the resultant reaction mixture showed characteristic stretching due to N–D bonds: ν (N-D) 2310 and 2375 cm⁻¹.

Study of Electronic Spectral Changes upon Addition of KO^tBu to 1b. To a 10^{-4} molar acetonitrile solution of 1b was added a pinch of KO^tBu. The color of the solution immediately changed from brown to reddish brown. The spectral changes were monitored over time.

Kinetic Study. A 50 mL round-bottom flask was charged with appropriate amounts of alcohol, catalyst, and base. To this mixture was added 10 mL of dry toluene, and the reaction mixture was placed in a oil bath preheated at 75 °C. A 0.1 mL aliquot was taken from the reaction vessel after a certain time interval and was monitored spectrophotometrically at 290 nm with appropriate dilution.

X-ray Crystallography. Suitable X-ray-quality crystals of L^{1a}·ClO₄ were obtained by slow evaporation of its acetonitrile solution. X-rayquality crystals of 1b, 2, $[3b](ClO_4)_2$, and $[4](ClO_4)_2$ were obtained by either slow evaporation or slow diffusion of their dichloromethanehexane solution. The X-ray single-crystal data of L^{1a}·ClO₄, 1b, 2, $[3b](ClO_4)_2$ and $[4](ClO_4)_2$ were collected with monochromated Mo K α radiation (λ = 0.71073 Å) on a Bruker SMART Apex II diffractometer equipped with a CCD area detector at 150(2) K. The crystals were positioned at 40 mm from the CCD, and the spots were measured using 5 and 10 s counting times, respectively. Data reduction was carried out using the SAINT-NT software package.²¹ Multiscan absorption correction was applied to all intensity data using the SADABS program.²² The structures were solved by a combination of direct methods with subsequent difference Fourier syntheses and refined by full-matrix least squares on F^2 using the SHELX-2013 suite.²³ All non-hydrogen atoms were refined with anisotropic thermal displacements. The crystal data together with refinement details are given in Table 6.

Computational Details. DFT calculations presented herein were carried out using the Gaussian 09 program package.²⁴ Geometry optimizations were performed without imposing geometric constraints. The vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and that there are only positive eigenvalues. All calculations were performed using the B3LYP functional with LANL2DZ basis set on Fe and 6-31G* on C, H, N, and Cl atoms.²⁵ The broken-symmetry approach^{26,27} was employed to establish the singlet state *S* = 0 of the compound(s). Mulliken spin densities were used for analysis of spin populations on ligand and metal centers.²⁸

ASSOCIATED CONTENT

Supporting Information

This material are available free of charge via the Internet at The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b02238.

ESI-MS spectra of ligands and Fe complexes, ¹H NMR spectra, ORTEP views, EPR spectra of the electrogenerated complexes, FMOs, and Cartesian coordinates of the optimized structures (PDF)

Accession Codes

CCDC 1550856–1550860 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail for N.D.P.: ndpaul@gmail.com.

ORCID 💿

Franc Meyer: 0000-0002-8613-7862 Nanda D. Paul: 0000-0002-8872-1413

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The research was supported by DST (Project: YSS/2015/ 001552). S.S. thanks the IIESTS, R.S. thanks the UGC-RGNF, and S.P. thanks the CSIR for fellowship support. Financial assistance from the IIESTS is acknowledged. P.B. thanks the CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT ref. UID/CTM/50011/2013), financed by national funds through the FCT/MEC and when appropriate cofinanced by FEDER under the PT2020 Partnership Agreement. We thank Prof. T. K. Paine (IACS, Kolkata), Prof. K. Pramanick (JU, Kolkata), and Dr. A. Saha (JU, Kolkata) for EPR experiments and Dr. S. Chatterjee (Srerampore College, Howrah) for helpful discussions. We also thank all the reviewers for their constructive suggestions during the revision period.

REFERENCES

(1) (a) Special Issue: Cooperative and Redox Non-Innocent Ligands in Directing Organometallic Reactivity. *Eur. J. Inorg. Chem.* **2012**, 340–342. DOI: 10.1002/ejic.201290001. (b) Forum on Redox-Active Ligands. *Inorg. Chem.* **2011**, *50*, 9737–9740. DOI: 10.1021/ic201881k. (c) Zanello, P.; Corsini, M. Homoleptic, mononuclear transition metal complexes of 1,2-dioxolenes: Updating their electrochemical-tostructural (X-ray) properties. *Coord. Chem. Rev.* **2006**, *250*, 2000– 2022. (d) Chaudhuri, P.; Wieghardt, K. Phenoxyl Radical Complexes. *Prog. Inorg. Chem.* **2002**, *50*, 151–216. (e) Jazdzewski, B. A.; Tolman, W. B. *Coord. Chem. Rev.* **2000**, 200-202, 633–685. (f) Pierpont, C. G.; Lange, C. W. The Chemistry of Transition Metal Complexes Containing Catechol and Semiquinone Ligands. *Prog. Inorg. Chem.* **1994**, *41*, 331–341. (g) Dzik, W. I.; van der Vlugt, J. I.; Reek, J. N. H.; de Bruin, B. Ligands that Store & Release Electrons during Catalysis. *Angew. Chem., Int. Ed.* **2011**, *50*, 3356–3358.

(2) (a) Kaim, W.; Schwederski, B. Non-innocent ligands in bioinorganic chemistry—An overview. *Coord. Chem. Rev.* 2010, 254, 1580–1588. (b) Que, L.; Tolman, W. B. Biologically inspired oxidation catalysis. *Nature* 2008, 455, 333–340. (c) Stubbe, J.; Van der Donk, W. A. Protein Radicals in Enzyme Catalysis. *Chem. Rev.* 1998, 98, 705–762.

(3) (a) Chirik, P. J.; Wieghardt, K. Radical Ligands Confer Nobility on Base-Metal Catalysts. Science 2010, 327, 794-795. (b) Broere, D. J. L.; Plessius, R.; van der Vlugt, J. I. New avenues for ligand-mediated processes - expanding metal reactivity by the use of redox-active catechol, o-aminophenol and o-phenylenediamine ligands. Chem. Soc. Rev. 2015, 44, 6886-6915. (c) Luca, O. R.; Crabtree, R. H. Redoxactive ligands in catalysis. Chem. Soc. Rev. 2013, 42, 1440-1459. (d) Lyaskovskyy, V.; de Bruin, B. Redox Non-Innocent Ligands: Versatile New Tools to Control Catalytic Reactions. ACS Catal. 2012, 2, 270-279. (e) de Bruin, B.; Gualco, P.; Paul, N. D. In Ligand Design In Metal Chemistry: Reactivity and Catalysis; Stradiotto, M., Lundgren, R., Eds.; Wiley: New York, in press. (f) Smith, A. L.; Hardcastle, K. I.; Soper, J. D. Redox-Active Ligand-Mediated Oxidative Addition and Reductive Elimination at Square Planar Cobalt(III): Multielectron Reactions for Cross-Coupling. J. Am. Chem. Soc. 2010, 132, 14358-14360. (g) Sylvester, K. J.; Chirik, P. J. Iron-Catalyzed, Hydrogen-Mediated Reductive Cyclization of 1,6-Enynes and Diynes: Evidence for Bis(imino)pyridine Ligand Participation. J. Am. Chem. Soc. 2009,

131, 8772-8774. (h) O'Reilly, M. E.; Veige, A. S. Trianionic pincer and pincer-type metal complexes and catalysts. Chem. Soc. Rev. 2014, 43, 6325-6369. (i) Nadif, S. S.; O'Reilly, M. E.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. Remote Multiproton Storage within a Pyrrolide-Pincer-Type Ligand. Angew. Chem., Int. Ed. 2015, 54, 15138-15142. (4) (a) Paul, N. D.; Rana, U.; Goswami, S.; Mondal, T. K.; Goswami, S. Azo Anion Radical Complex of Rhodium as a Molecular Memory Switching Device: Isolation, Characterization, and Evaluation of Current-Voltage Characteristics. J. Am. Chem. Soc. 2012, 134, 6520-6523. (b) Goswami, S.; Sengupta, D.; Paul, N. D.; Mondal, T. K.; Goswami, S. Redox Non-Innocence of Coordinated 2-(Arylazo) Pyridines in Iridium Complexes: Characterization of Redox Series and an Insight into Voltage-Induced Current Characteristics. Chem. - Eur. J. 2014, 20, 6103-6111. (c) Bandyopadhyay, A.; Sahu, S.; Higuchi, M. Tuning of Nonvolatile Bipolar Memristive Switching in Co(III) Polymer with an Extended Azo Aromatic Ligand. J. Am. Chem. Soc. 2011, 133, 1168-1171. (d) Lee, J.; Lee, E.; Kim, S.; Bang, G. S.; Shultz, D. A.; Schmidt, R. D.; Forbes, M. D. E.; Lee, H. Nitronyl Nitroxide Radicals as Organic Memory Elements with Both n- and p-Type Properties. Angew. Chem., Int. Ed. 2011, 50, 4414-4418. (e) Seo, K.; Konchenko, A. V.; Lee, J.; Bang, G. S.; Lee, H. Molecular Conductance Switch-On of Single Ruthenium Complex Molecules. J. Am. Chem. Soc. 2008, 130, 2553-2559.

(5) (a) Poddel'sky, A. I.; Cherkasov, V. K.; Abakumov, G. A. Transition metal complexes with bulky 4,6-di-tert-butyl-N-aryl(alkyl)o-iminobenzoquinonato ligands: Structure, EPR and magnetism. Coord. Chem. Rev. 2009, 253, 291-324. (b) Herebian, D.; Wieghardt, K. E.; Neese, F. Analysis and Interpretation of Metal-Radical Coupling in a Series of Square Planar Nickel Complexes: Correlated Ab Initio and Density Functional Investigation of [Ni(L^{ISQ})₂] (L^{ISQ}=3,5-di-*tert*-butyl-o-diiminobenzosemiquinonate(1-)). J. Am. Chem. Soc. 2003, 125, 10997-11005. (c) Metcalfe, R. A.; Dodsworth, E. S.; Fielder, S. S.; Stufkens, D. J.; Lever, A. B. P.; Pietro, W. J. Influence of Remote Ligand Lone Pairs on the Electronic Structure and Spectrum of Bis(bipyridine)ruthenium(II) 3,4-Diamino-3',4'-diimino-3',4'-dihydrobiphenyl. Tuning by External Donors and Acceptors. Inorg. Chem. 1996, 35, 7741-7750. (d) Mandal, S.; Paul, N. D.; Banerjee, P.; Mondal, T. K.; Goswami, S. 1,4-Alkyl migration associated with simultaneous S-C bond cleavage and N-C bond formation in platinum complexes of 2-aminothioethers. Characterization of intramolecular interligand charge transfer phenomenon. Dalton Trans. 2010, 39, 2717-2726. (e) Herebian, D.; Bothe, E.; Neese, F.; Weyhermüller, T.; Wieghardt, K. Molecular and Electronic Structures of Bis-(o-diiminobenzosemiquinonato)metal(II) Complexes (Ni, Pd, Pt), Their Monocations and -Anions, and of Dimeric Dications Containing Weak Metal-Metal Bonds. J. Am. Chem. Soc. 2003, 125, 9116-9128. (f) Chun, H.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. Octahedral (cis-Cyclam)iron(III) Complexes with $O_{J}N$ -Coordinated o-Iminosemiquinonate(1-) π Radicals and o-Imidophenolate(2-) Anions. Inorg. Chem. 2002, 41, 5091-5099. (g) Mukherjee, M.; Weyhermüller, T.; Bill, E.; Wieghardt, K.; Chaudhuri, P. Tuning of Spin Transition in Radical-Containing Iron(III) Complexes by Remote Ligand Substituents. Inorg. Chem. 2005, 44, 7099-7108.

(6) (a) Broere, D. L. J.; de Bruin, B.; Reek, J. N. H.; Lutz, M.; Dechert, S.; van der Vlugt, J. I. Intramolecular Redox-Active Ligand-to-Substrate Single-Electron Transfer: Radical Reactivity with a Palladium(II) Complex. J. Am. Chem. Soc. 2014, 136, 11574–11577. (b) Breitenfeld, J.; Ruiz, J.; Wodrich, M. D.; Hu, X. Bimetallic Oxidative Addition Involving Radical Intermediates in Nickel-Catalyzed Alkyl–Alkyl Kumada Coupling Reactions. J. Am. Chem. Soc. 2013, 135, 12004–12012. (c) Ren, P.; Vechorkin, O.; Allmen, K.; Scopelliti, R.; Hu, X. A Structure–Activity Study of Ni-Catalyzed Alkyl–Alkyl Kumada Coupling. Improved Catalysts for Coupling of Secondary Alkyl Halides. J. Am. Chem. Soc. 2011, 133, 7084–7095. (d) Nguyen, A. I.; Blackmore, K. J.; Carter, S. M.; Zarkesh, R. A.; Heyduk, A. F. One- and Two-Electron Reactivity of a Tantalum(V) Complex with a Redox-Active Tris(amido) Ligand. J. Am. Chem. Soc. 2009, 131, 3307–3316. (e) Munhá, R. F.; Zarkesh, R. A.; Heyduk, A. F. Tuning the Electronic and Steric Parameters of a Redox-Active Tris(amido) Ligand. Inorg. Chem. 2013, 52, 11244-11255. (f) Szigethy, G.; Shaffer, D. W.; Heyduk, A. F. Coordination Effects on Electron Distributions for Rhodium Complexes of the Redox-Active Bis(3,5-di-tert-butyl-2-phenolate) amide Ligand. Inorg. Chem. 2012, 51, 12606-12618. (g) Paretzki, A.; Bubrin, M.; Fiedler, J.; Zàliš, S.; Kaim, W. Correlated Coordination and Redox Activity of a Hemilabile Noninnocent Ligand in Nickel Complexes. Chem. - Eur. J. 2014, 20, 5414-5422. (h) Ye, S.; Sarkar, B.; Lissner, F.; Schleid, Th.; van Slageren, J.; Fiedler, J.; Kaim, W. Three-Spin System with a Twist: A Bis(semiquinonato)copper Complex with a Nonplanar Configuration at the Copper(II) Center. Angew. Chem., Int. Ed. 2005, 44, 2103-2106. (i) Wolff, C.; Gottschlich, A.; England, J.; Wieghardt, K.; Saak, W.; Haase, D.; Beckhaus, R. Molecular and Electronic Structures of Mononuclear and Dinuclear Titanium Complexes Containing π -Radical Anions of 2,2-Bipyridineand 1,10-Phenanthroline: An Experimental and DFT Computational Study. Inorg. Chem. 2015, 54, 4811-4820.

(7) (a) Chirik, P. J. Iron- and Cobalt-Catalyzed Alkene Hydrogenation: Catalysis with Both Redox-Active and Strong Field Ligands. Acc. Chem. Res. 2015, 48, 1687-1695. (b) Schuster, C. H.; Diao, T.; Pappas, I.; Chirik, P. J. Bench-Stable, Substrate-Activated Cobalt Carboxylate Pre-Catalysts for Alkene Hydrosilylation with Tertiary Silanes. ACS Catal. 2016, 6, 2632-2636. (c) Schmidt, V. A.; Hoyt, J. M.; Margulieux, G. W.; Chirik, P. J. Cobalt-Catalyzed $\left[2\pi + 2\pi\right]$ Cycloadditions of Alkenes: Scope, Mechanism, and Elucidation of Electronic Structure of Catalytic Intermediates. J. Am. Chem. Soc. 2015, 137, 7903-7914. (d) Atienza, C. C. H.; Diao, T.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G. P.; Boyer, J. L.; Roy, A. K.; Chirik, P. J. Bis(imino)pyridine Cobalt-Catalyzed Dehydrogenative Silvlation of Alkenes: Scope, Mechanism, and Origins of Selective Allylsilane Formation. J. Am. Chem. Soc. 2014, 136, 12108-12118. (e) Darmon, J. M.; Stieber, S. C. E.; Sylvester, K. T.; Fernández, I.; Lobkovsky, E.; Semproni, S. P.; Bill, E.; Wieghardt, K.; DeBeer, S.; Chirik, P. J. Oxidative Addition of Carbon-Carbon Bonds with a Redox-Active Bis(imino)pyridine Iron Complex. J. Am. Chem. Soc. 2012, 134, 17125-17137. (f) Hojilla Atienza, C. C.; Tondreau, A. M.; Weller, K. J.; Lewis, K. M.; Cruse, R. W.; Nye, S. A.; Boyer, J. L.; Delis, J. G. P.; Chirik, P. J. High-Selectivity Bis(imino)pyridine Iron Catalysts for the Hydrosilylation of 1,2,4-Trivinylcyclohexane. ACS Catal. 2012, 2, 2169-2172.

(8) (a) Jana, R.; Lissner, F.; Schwederski, B.; Fiedler, J.; Kaim, W. A Ligand-Bridged Heterotetranuclear (Fe₂Cu₂) Redox System with Fc/ Fc⁺ and Radical Ion Intermediates. Organometallics 2013, 32, 5879-5886. (b) Baumann, F.; Kaim, W.; Denninger, G.; Kümmerer, H.; Fiedler, J. Widely Separated Reduction Processes of abpy-Coupled Areneosmium(II) Reaction Centers (abpy = 2,2'-Azobispyridine): Stabilization of the Radical Intermediate and of the Os⁰Os^{II} State. Organometallics 2005, 24, 1966-1973. (c) Sarkar, B.; Kaim, W.; Fiedler, J.; Duboc, C. Molecule-Bridged Mixed-Valent Intermediates Involving the Ru^I Oxidation State. J. Am. Chem. Soc. 2004, 126, 14706-14707. (d) Dogan, A.; Sarkar, B.; Klein, A.; Lissner, F.; Schleid, T.; Fiedler, J.; Záliš, S.; Jain, V. K.; Kaim, W. Complex Reduction Chemistry of (abpy)PtCl₂, abpy = $2_{2}2'$ -Azobispyridine: Formation of Cyclic $[(\mu,\eta^2;\eta^1\text{-abpy})\text{PtCl}]_2^{2+}$ with a New Coordination Mode for abpy and a Near-Infrared Ligand-to-Ligand Intervalence Charge Transfer Absorption of the One-Electron Reduced State. Inorg. Chem. 2004, 43, 5973-5980. (e) Kaim, W.; Reinhardt, R.; Greulich, S.; Fiedler, J. Resolving the Two-Electron Process for the Couple $[(C_5Me_5)M(NN)Cl]^+/[(C_5Me_5)M(NN)] (M = Rh, Ir) into Two$ One-Electron Steps Using the 2,2'-Azobis(pyridine) NN Ligand, Fast Scan Cyclovoltammetry, and Spectroelectrochemistry: Detection of Radicals instead of M^{II} Intermediates. Organometallics 2003, 22, 2240-2244. (f) Frantz, S.; Hartmann, H.; Doslik, N.; Wanner, M.; Kaim, W.; Kümmerer, H.; Denninger, G.; Barra, A.; Duboc-Toia, C.; Fiedler, J.; Ciofini, I.; Urban, C.; Kaupp, M. Multifrequency EPR Study and Density Functional g-Tensor Calculations of Persistent Organorhenium Radical Complexes. J. Am. Chem. Soc. 2002, 124, 10563-10571. (g) Doslik, N.; Sixt, T.; Kaim, W. The First Structural

Characterization of an Azoaromatic Radical Anion Stabilized by Dicopper(I) Coordination. *Angew. Chem., Int. Ed.* **1998**, 37, 2403–2404.

(9) (a) Sengupta, D.; Saha Chowdhury, N.; Samanta, S.; Ghosh, P.; Seth, S. K.; Demeshko, S.; Meyer, F.; Goswami, S. Regioselective ortho Amination of Coordinated 2-(Arylazo)pyridine. Isolation of Monoradical Palladium Complexes of a New Series of Azo-Aromatic Pincer Ligands. Inorg. Chem. 2015, 54, 11465-11476. (b) Sengupta, D.; Ghosh, P.; Chatterjee, T.; Datta, H.; Paul, N. D.; Goswami, S. Ligand-Centered Redox in Nickel(II) Complexes of 2-(Arylazo)pyridine and Isolation of 2-Pyridyl-Substituted Triaryl Hydrazines via Catalytic N-Arylation of Azo-Function. Inorg. Chem. 2014, 53, 12002-12013. (c) Ghosh, P.; Samanta, S.; Roy, S. K.; Demeshko, S.; Meyer, F.; Goswami, S. Introducing a New Azoaromatic Pincer Ligand. Isolation and Characterization of Redox Events in Its Ferrous Complexes. Inorg. Chem. 2014, 53, 4678-4686. (d) Joy, S.; Krämer, T.; Paul, N. D.; Banerjee, P.; McGrady, J. E.; Goswami, S. Isolation and Assessment of the Molecular and Electronic Structures of Azo-Anion-Radical Complexes of Chromium and Molybdenum. Experimental and Theoretical Characterization of Complete Electron-Transfer Series. Inorg. Chem. 2011, 50, 9993-10004. (e) Paul, N. D.; Samanta, S.; Mondal, T. K.; Goswami, S. Examples of Reductive Azo Cleavage and Oxidative Azo Bond Formation on Re₂(CO)₁₀ Template: Isolation and Characterization of Re(III) Complexes of New Azo-Aromatic Ligands. Inorg. Chem. 2011, 50, 7886-7893. (f) Paul, N. D.; Samanta, S.; Goswami, S. Redox Induced Electron Transfer in Doublet Azo-Anion Diradical Rhenium(II) Complexes. Characterization of Complete Electron Transfer Series. Inorg. Chem. 2010, 49, 2649-2655. (g) Paul, N. D.; Krämer, T.; McGrady, J. E.; Goswami, S. Dioxygen Activation by Mixed-valent Dirhodium Complexes of Redox Non-innocent Azoaromatic Ligands. Chem. Commun. 2010, 46, 7124-7126.

(10) (a) Shivakumar, M.; Pramanik, K.; Ghosh, P.; Chakravorty, A. Synthesis and Characterisation of A Pair of Azo Anion Radicals Bonded to Ruthenium(II). Chem. Commun. 1998, 2103-2104. (b) Shivakumar, M.; Pramanik, K.; Ghosh, P.; Chakravorty, A. Isolation and Structure of the First Azo Anion Radical Complexes of Ruthenium. Inorg. Chem. 1998, 37, 5968-5969. (c) Pramanik, K.; Shivakumar, M.; Ghosh, P.; Chakravorty, A. Azo Anion Radical Complexes of Osmium and Related Nonradical Species. Inorg. Chem. 2000, 39, 195-199. (d) Pfeiffer, C. R.; Fowler, D. A.; Atwood, J. L. Selective Complexation in Three Component Cocrystals Composed of Pyrogallol[4]arene and Fluorescent Probes Pyrene and 1-(2-Pyridylazo)-2-naphthol. Cryst. Growth Des. 2015, 15, 3992-3998. (e) Hotze, A. C. G.; van der Geer, E. P. L.; Caspers, S. E.; Kooijman, H.; Spek, A. L.; Haasnoot, J. G.; Reedijk, J. Coordination of 9-Ethylguanine to the Mixed-Ligand Compound α -[Ru(azpy)(bpy)Cl₂] (azpy = 2-Phenylazopyridine and bpy = 2,2'-Bipyridine). An Unprecedented Ligand Positional Shift, Correlated to the Cytotoxicity of This Type of $[RuL_2Cl_2]$ (with L = azpy or bpy) Complex. Inorg. Chem. 2004, 43, 4935-4943. (f) Velders, A. H.; Kooijman, H.; Spek, A. L.; Haasnoot, J. G.; de Vos, D.; Reedijk, J. Strong Differences in the in Vitro Cytotoxicity of Three Isomeric Dichlorobis(2phenylazopyridine)ruthenium(II) Complexes. Inorg. Chem. 2000, 39, 2966–2967. (g) Majumder, P.; Baksi, S.; Halder, S.; Tadesse, H.; Blake, A. J.; Drew, M. G. B.; Bhattacharya, S. Formation of Organorhodium Complexes via C-H Bond Activation of 1,3-Di(phenylazo)benzene. Dalton Trans. 2011, 40, 5423-5425.

(11) Sengupta, D.; Bhattacharjee, R.; Pramanick, R.; Rath, S. P.; Saha Chowdhury, N.; Datta, A.; Goswami, S. Exclusively Ligand-Mediated Catalytic Dehydrogenation of Alcohols. *Inorg. Chem.* **2016**, *55*, 9602–9610.

(12) (a) Song, H.; Kang, B.; Hong, S. H. Fe-Catalyzed Acceptorless Dehydrogenation of Secondary Benzylic Alcohols. *ACS Catal.* **2014**, *4*, 2889–2895. (b) Weiss, C. J.; Das, P.; Miller, D. L.; Helm, M. L.; Appel, A. M. Catalytic Oxidation of Alcohol via Nickel Phosphine Complexes with Pendant Amines. *ACS Catal.* **2014**, *4*, 2951–2958. (c) Steves, J. E.; Stahl, S. S. Copper(I)/ABNO-Catalyzed Aerobic Alcohol Oxidation: Alleviating Steric and Electronic Constraints of Cu/TEMPO Catalyst Systems. J. Am. Chem. Soc. 2013, 135, 15742-15745. (d) Hoover, J. M.; Stahl, S. S. Highly Practical Copper(I)/ TEMPO Catalyst System for Chemoselective Aerobic Oxidation of Primary Alcohols. J. Am. Chem. Soc. 2011, 133, 16901-16910. (e) Zhang, G.; Vasudevan, K. V.; Scott, B. L.; Hanson, S. K. J. Am. Chem. Soc. 2013, 135, 8668-8681. (f) Bianchini, C.; Shen, P. K. Palladium-Based Electrocatalysts for Alcohol Oxidation in Half Cells and in Direct Alcohol Fuel Cells. Chem. Rev. 2009, 109, 4183-4206. (g) Sikari, R.; Sinha, S.; Jash, U.; Das, S.; Brandaõ, P.; de Bruin, B.; Paul, N. D. Deprotonation Induced Ligand Oxidation in a Ni^{II} Complex of a Redox Noninnocent N1-(2-Aminophenyl)benzene-1,2diamine and Its Use in Catalytic Alcohol Oxidation. Inorg. Chem. 2016, 55, 6114-6123. (h) Parua, S.; Das, S.; Sikari, R.; Sinha, S.; Paul, N. D. One-Pot Cascade Synthesis of Quinazolin-4(3H)-ones via Nickel-Catalyzed Dehydrogenative Coupling of o-Aminobenzamides with Alcohols. J. Org. Chem. 2017, 82, 7165-7175. (i) Ma, Y.; Du, Z.; Liu, J.; Xia, F.; Xu, J. Selective Oxidative C-C Bond Cleavage of a Lignin Model Compound in the Presence of Acetic Acid with a Vanadium Catalyst. Green Chem. 2015, 17, 4968. (j) Ray, R.; Chandra, S.; Maiti, D.; Lahiri, G. K. Simple and Efficient Ruthenium-Catalyzed Oxidation of Primary Alcohols with Molecular Oxygen. Chem. - Eur. J. 2016, 22, 8814-8822.

(13) (a) Engel, Y.; Dahan, A.; Rozenshine-Kemelmakher, E.; Gozin, M. Phenanthroline-Derived Ratiometric Chemosensor for Ureas. J. Org. Chem. 2007, 72, 2318–2328. (b) Kumar, P.; Madyal, R. S.; Joshi, U.; Gaikar, V. J. Design and Synthesis of Polymer-Bound Penta-aza Ligand for Selective Adsorptive Separation of Cobalt(II) from Zirconium(IV). Ind. Eng. Chem. Res. 2011, 50, 8195–8203.

(14) Widger, L. R.; Jiang, Y.; Siegler, M. A.; Kumar, D.; Latifi, R.; de Visser, S. P.; Jameson, G. N. L.; Goldberg, D. P. Synthesis and Ligand Non-Innocence of Thiolate-Ligated (N₄S) Iron(II) and Nickel(II) Bis(imino)pyridine Complexes. *Inorg. Chem.* **2013**, *52*, 10467–10480. (15) (a) de Bruin, B.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. Molecular and Electronic Structures of Bis(pyridine-2,6-diimine)metal Complexes [ML₂](PF₆)_n (n = 0, 1, 2, 3; M = Mn, Fe, Co, Ni, Cu, Zn). *Inorg. Chem.* **2000**, *39*, 2936–2947.

(16) (a) Yi, H.; Jutand, A.; Lei, A. Evidence for the Interaction Between 'BuOK and 1,10-Phenanthroline to form the 1,10-Phenanthroline Radical Anion: a Key Step for the Activation of Aryl Bromides by Electron Transfer. *Chem. Commun.* 2015, *51*, 545–548.
(b) Cuthbertson, J.; Gray, V. J.; Wilden, J. D. Observations on Transition Metal Free Biaryl Coupling: Potassium tert-Butoxide Alone Promotes the Reaction without Diamine or Phenanthroline Catalysts. *Chem. Commun.* 2014, *50*, 2575–2578. (c) Barham, J. P.; Coulthard, G.; Emery, K. J.; Doni, E.; Cumine, F.; Nocera, G.; John, M. P.; Berlouis, L. E. A.; McGuire, T.; Tuttle, T.; Murphy, J. A. KO'Bu: A Privileged Reagent for Electron Transfer Reactions? *J. Am. Chem. Soc.* 2016, *138*, 7402–7410.

(17) Wang, J.; Liu, C.; Yuan, J.; Lei, L. Transition-metal-free aerobic oxidation of primary alcohols to carboxylic acids. *New J. Chem.* **2013**, 37, 1700–1703.

(18) (a) Chaudhuri, P.; Hess, M.; Müller, J.; Hildenbrand, K.; Bill, E.; Weyhermüller, T.; Wieghardt, K. Aerobic Oxidation of Primary Alcohols (Including Methanol) by Copper(II)- and Zinc(II)-Phenoxyl Radical Catalysts. J. Am. Chem. Soc. 1999, 121, 9599-9610. (b) Halfen, J. A.; Young, V. G.; Tolman, W. B. Modeling of the Chemistry of the Active Site of Galactose Oxidase. Angew. Chem., Int. Ed. Engl. 1996, 35, 1687-1690. (c) Halfen, J. A.; Jazdzewski, B. A.; Mahapatra, S.; Berreau, L. M.; Wilkinson, E. C.; Que, L.; Tolman, W. B. Synthetic Models of the Inactive Copper(II)-Tyrosinate and Active Copper-(II)-Tyrosyl Radical Forms of Galactose and Glyoxal Oxidases. J. Am. Chem. Soc. 1997, 119, 8217-8227. (d) McCann, S. D.; Stahl, S. S. Mechanism of Copper/Azodicarboxylate-Catalyzed Aerobic Alcohol Oxidation: Evidence for Uncooperative Catalysis. J. Am. Chem. Soc. 2016, 138, 199-206. (e) Markó, I. E.; Giles, P. R.; Tsukazaki, M.; Brown, S. M.; Urch, C. J. Copper-Catalyzed Oxidation of Alcohols to Aldehydes and Ketones: An Efficient, Aerobic Alternative. Science 1996, 274, 2044-2046.

(19) Goswami, S.; Mukherjee, R. N.; Chakravorty, A. Chemistry of ruthenium. 12. Reactions of bidentate ligands with diaquabis[2-(arylazo)pyridine]ruthenium(II) cation. Stereoretentive synthesis of tris chelates and their characterization: metal oxidation, ligand reduction, and spectroelectrochemical correlation. *Inorg. Chem.* **1983**, *22*, 2825–2832.

(20) Adhikary, J.; Chakraborty, P.; Das, S.; Chattopadhyay, T.; Bauza, A.; Chattopadhyay, S. K.; Ghosh, B.; Mautner, F. A.; Frontera, A.; Das, D. A Combined Experimental and Theoretical Investigation on the Role of Halide Ligands on the Catecholase-like Activity of Mononuclear Nickel(II) Complexes with a Phenol-Based Tridentate Ligand. *Inorg. Chem.* **2013**, *52*, 13442–13452.

(21) Bruker SAINT-plus; Bruker AXS Inc., Madison, WI, USA, 2007.
(22) (a) Sheldrick, G. M. SHELXS-97, a Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, 1997.
(b) Sheldrick, G. M. SHELXL-97, a Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.

(23) Sheldrick, G. M. Acta Crystallogr., Sect. A: Found. Crystallogr. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112–122.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 09, Revision A.02; Gaussian, Inc., Wallingford, CT, 2010.

(25) (a) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 1993, 98, 5648-5652. (b) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B: Condens. Matter Mater. Phys. 1988, 37, 785-789.
(c) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. Can. J. Phys. 1980, 58, 1200-1211. (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. J. Phys. Chem. 1994, 98, 11623-11627.

(26) Ginsberg, A. P. Magnetic exchange in transition metal complexes. 12. Calculation of cluster exchange coupling constants with the X. alpha.-scattered wave method. *J. Am. Chem. Soc.* **1980**, *102*, 111–117.

(27) (a) Noodleman, L.; Case, D. A.; Aizman, A. Broken symmetry analysis of spin coupling in iron-sulfur clusters. *J. Am. Chem. Soc.* **1988**, *110*, 1001–1005. (b) Noodleman, L.; Davidson, E. R. Ligand spin polarization and antiferromagnetic coupling in transition metal dimers. *Chem. Phys.* **1986**, *109*, 131–143. (c) Noodleman, L.; Norman, J. G., Jr.; Osborne, J. H.; Aizman, C.; Case, D. A. Models for ferredoxins: electronic structures of iron-sulfur clusters with one, two, and four iron atoms. *J. Am. Chem. Soc.* **1985**, *107*, 3418–3426. (d) Noodleman, L. Valence bond description of antiferromagnetic coupling in transition metal dimers. *J. Chem. Phys.* **1981**, *74*, 5737–5743.

(28) Mulliken, R. S. Electronic Population Analysis on LCAO-MO Molecular Wave Functions. J. Chem. Phys. **1955**, 23, 1833-1840.