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Oxidation of Alcohols and Activated Alkanes with Lewis Acid-Activated TEMPO

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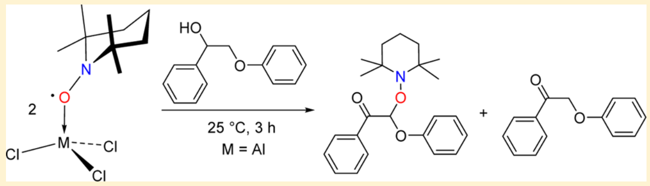
Supporting Information

ABSTRACT: The reactivity of $MCl_3(\eta^1\text{-TEMPO})$ (M = Fe, **1**; Al, **2**; TEMPO = 2,2,6,6-tetramethylpiperidine-*N*-oxyl) with a variety of alcohols, including 3,4-dimethoxybenzyl alcohol, 1-phenyl-2-phenoxyethanol, and 1,2-diphenyl-2-methoxyethanol, was investigated using NMR spectroscopy and mass spectrometry. Complex **1** was effective in cleanly converting these substrates to the corresponding aldehyde or ketone. Complex **2** was also able to oxidize these substrates; however, in a few instances the products of overoxidation were also observed. Oxidation of activated alkanes, such as xanthene, by **1** or **2** suggests that the reactions proceed via an initial 1-electron concerted proton−electron transfer (CPET) event. Finally, reaction of TEMPO with $FeBr_3$ in Et_2O results in the formation of a mixture of $FeBr_3(\eta^1\text{-TEMPOH})$ (**23**) and $[FeBr_2(\eta^1\text{-TEMPOH})]_2(\mu\text{-O})$ (**24**), via oxidation of the solvent, Et_2O.



■ INTRODUCTION

N-Oxyl radicals, such as TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidine-*N*-oxyl) and ABNO (ABNO = 9-azabicyclo[3.3.1]nonane *N*-oxyl), are widely used in a variety of organic oxidations. In particular, they have proven excellent reagents for the selective oxidation of primary alcohols,[1−5] secondary alcohols,[6,7] primary amines,[8] and the α-oxyamination of aldehydes.[9] More recently, TEMPO has also found use in the depolymerization of lignin. For example, Stahl and co-workers demonstrated that efficient oxidation of the alcohol functionalities in lignin[10] can be achieved with the 4-acetamido-TEMPO/HNO_3/HCl system, wherein the active oxidant is likely [4-acetamido-TEMPO]$^+$. Stephenson and co-workers report a similar lignin oxidation process, in which the benzylic alcohol functionalities are oxidized by [4-acetamido-TEMPO][BF_4].[11] Hanson and co-workers have also had considerable success in effecting the degradation of lignin model compounds by using a TEMPO-based oxidant.[12,13] For example, they reported that the CuCl/TEMPO and CuOTf/2,6-lutidine/TEMPO catalyst systems could oxidatively cleave both a β-O-4 lignin model and β-1 lignin model, using oxygen as the terminal oxidant. While promising, these Cu/TEMPO protocols required harsh conditions and long reaction times, which is significant because several lignin functional groups are not stable at elevated temperatures.[11]

Previously, our research group reported the use of the Lewis acids $FeCl_3$ and $AlCl_3$, to activate TEMPO toward the oxidation of alcohols.[14] The resulting $MCl_3(\eta^1\text{-TEMPO})$ (M = Fe, **1**; Al, **2**) adducts were observed to quickly oxidize both 1° and 2° alcohols, forming the corresponding carbonyl compounds under mild conditions. Complexes **1** and **2** are also capable of oxidizing 9,10-dihydroanthracene, although this oxidation is much slower than those performed with alcohol substrates. Importantly, complexes **1** and **2** appear to be more reactive than other TEMPO-based systems, oxidizing alcohols within minutes at room temperature. While the $MCl_3(\eta^1\text{-TEMPO})$ system appears to have some advantages over other TEMPO protocols, there are still several mechanistic questions that remain unanswered. In particular, previous work on the Cu/TEMPO system suggests that the reaction proceeds via a concerted $2e^-$ oxidation, wherein a Cu-bound alcohol is simultaneously oxidized by TEMPO and Cu(II).[15] In contrast, preliminary mechanistic experiments with $MCl_3(\eta^1\text{-TEMPO})$ suggest that the reaction proceeds via an initial $1e^-$ hydrogen atom transfer event, which apparently makes this system unique among TEMPO-containing oxidants. As a result, we wanted to solidify our proposed mechanism by exploring the reactivity of $MCl_3(\eta^1\text{-TEMPO})$ with a variety of mechanistic probes, including activated alkanes and radical clocks. Herein, we report the reactivity of **1** and **2** toward a variety of alcohols and activated alkanes, including xanthene.[10,16−24] The latter substrate is significant, because its reactivity confirms that these oxidations can proceed via a concerted proton coupled electron transfer (CPET) step, as was previously surmised.[14] To test the role of the Lewis acid in activating the TEMPO moiety, we also explored the reactivity of TEMPO with $FeBr_3$ in Et_2O.

■ RESULTS AND DISCUSSION

Exploration of Substrate Scope. Reaction of $MCl_3(\eta^1\text{-TEMPO})$ (M = Fe, **1**; Al, **2**) with 3,4-dimethoxybenzyl alcohol (**3**), in Et_2O (for **1**) or CD_2Cl_2 (for **2**), results in the complete consumption of the alcohol within 10 min at room temperature and formation of 3,4-dimethoxybenzaldehyde (**4**) in good yields (Table 1, entry 1). For both reactions, compound **4** is the only organic product observable in the reaction mixture by ^{1}H NMR spectroscopy.[25] Similarly, oxidation of 1-phenyl-2-phenoxyetha-

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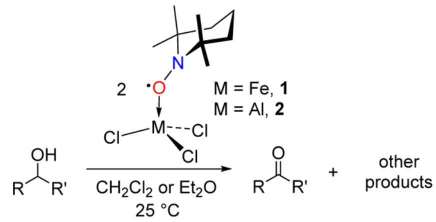
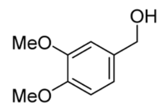
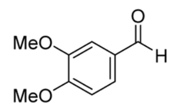
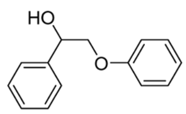
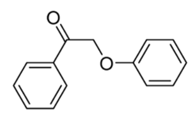
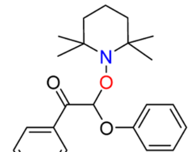
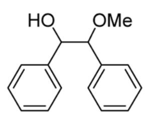
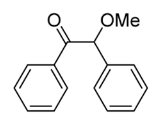
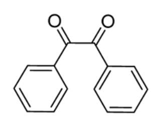
Table 1. Oxidation of Lignin Models by Complexes 1 and 2[a]



Entry	Substrate	% Conversion Fe	% Conversion Al	Product	% Yield Fe	% Yield Al
1	 **3**	100	100	 **4**	75	99
2	 **5**	100	100	 **6**	65	75
				 **7**	0	5
3	 **8**	100	77	 **9**	75	0
				 **10**	0	54

[a]Yields determined by ^{1}H NMR spectroscopy.

nol (**5**), which has been previously employed as a *β*-*O*-4 lignin model compound,[21−23] with complex **1** results in complete consumption of the alcohol within 3 h, and formation of 2-phenoxyacetophenone (**6**) in 65% yield (Table 1, entry 2). Complex **2** also oxidizes **5** to **6** (75% yield); however, a small amount of a new product is also observed in this transformation, namely, 2-(2,2,6,6-tetramethylpiperidine-*N*-oxyl)-2-phenoxyacetophenone (**7**), which is produced in 5% yield (Table 1, entry 2). We suggest that this product is formed through further oxidation of compound **6** by complex **2**, which results in formation of an *α*-keto radical, via H atom abstraction. The *α*-keto radical is subsequently quenched by coupling to free TEMPO, resulting in the formation of the new C−O bond. The formation of **7** is perhaps not surprising considering that the strength of the C−H bond abstracted in **6** (80.6 kcal/mol in DMSO)[26] is identical to the benzylic C−H bond enthalpy of 9,10-dihydroanthracene (80.6 kcal/mol in DMSO),[14,27] which both complexes **1** and **2** can readily oxidize. Interestingly, a related *α*-oxyamination using TEMPO has been previously described for enamines, and likely occurs via a similar mechanism.[9]

We also explored the reaction of complexes **1** and **2** with 1,2-diphenyl-2-methoxyethanol (**8**), a common *β*-1 lignin model compound.[10,12,21] Oxidation of **8** with complex **1** results in complete consumption of the starting material and formation of 2-methoxy-1,2-diphenylethanone (**9**) in 75% yield (Table 1, entry 3). No other oxidation products were observed in the reaction mixture, according to ^{1}H NMR spectroscopy. In contrast, reaction of **2** with **8** does not result in the formation of **9**. Instead, the major organic product formed in the reaction is benzil (**10**) in 54% yield (77% conversion; Table 1, entry 3). We suggest that formation of benzil occurs via hydrogen abstraction of the transiently formed **9** by complex **2**, which results in the formation of an *α*-keto radical stabilized by the captodative effect.[28] The *α*-keto radical is then quenched by TEMPO, resulting in the formation of a new C−O bond. This species then forms benzil by release of methoxy and piperidyl radicals. Interestingly, TEMPO is known to function as an O atom source via N−O bond cleavage and release of the piperidyl radical.[29] For

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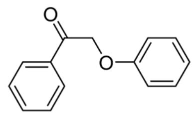
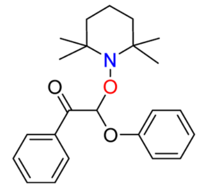
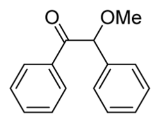
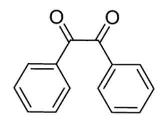
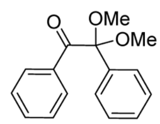
Table 2. Oxidation of Selected Substrates by Complexes 1 and 2[a]

Entry	Substrate	% Conversion		Product	% Yield	
		Fe	Al		Fe	Al
4	 **6**	27	96	 **7**	3	48
5	 **9**	0	89	 **10**	0	53
				 **11**	0	16

[a]Yields determined by ^{1}H NMR spectroscopy.

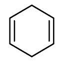
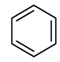
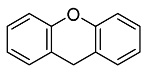
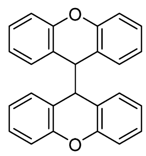
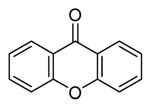
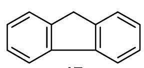
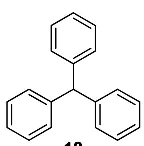
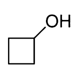
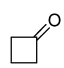
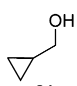
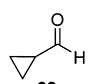
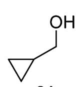
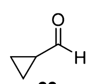
comparison, Hanson and co-workers reported that oxidation of **8** with O_2, in the presence of 10 mol % CuCl and 30 mol % TEMPO at 100 °C in pyridine, resulted in formation of benzaldehyde (84%) and methyl benzoate (88%).[12] We do not observe either of these products, which suggests that different mechanisms are operative in the two systems.

The viability of ketones **6** and **9** to act as the substrates for the formation of **7** and **10** was confirmed by their independent reaction with complexes **1** and **2**. Thus, reaction of 2 equiv of **2** with **6** in CH_2Cl_2 results in almost complete consumption of the starting material (96% conversion) after only 3 h, and production of the α-oxyamination product in 48% yield (Table 2, entry 4). In contrast, reaction of **6** with 2 equiv of **1** in Et_2O for 18 h left the starting material largely unreacted and produced **7** in only 3% yield, according to ^{1}H NMR spectroscopy (Table 2, entry 4). Oxidation of **9** by complex **2** in CH_2Cl_2 at room temperature for 15 h results in the formation of benzil (**10**) (53% yield) and 2,2-dimethoxy-2-phenylacetophenone (**11**) (16% yield), demonstrating that 2-methoxy-1,2-diphenylethanone (**9**) is a viable precursor to compound **10** (Table 2, entry 5). Compound **11** is probably formed by a Lewis acid-catalyzed reaction of **10** with methanol.[30−32] Notably, there is no reaction observed between complex **1** and **9** in CH_2Cl_2 after 15 h of stirring (Table 2, entry 5), which is consistent with the reactivity observed between **1** and **8** (Table 1, entry 3).

Mechanistic Studies. Previously, we argued that the first step in the oxidation of substrate by complexes **1** and **2** was a concerted proton−electron transfer (CPET) event.[14] To further evaluate this hypothesis, and better understand the reactivity of complexes **1** and **2** toward alcohols, we explored the reactivity of $MCl_3(\eta^1$-TEMPO) with a variety of activated alkanes. Reaction of 1,4-cyclohexadiene (**12**) with 2 equiv of **1** in toluene-d_8 results in almost complete consumption of **12** within 2 h, and formation of benzene in 82% yield (Table 3, entry 6). Similarly, reaction of **12** with 2 equiv of **2** in CD_2Cl_2 results in the complete conversion of **12** into benzene within 15 min (Table 3, entry 6), according to ^{1}H NMR spectroscopy. Oxidation of xanthene (**14**) with 2 equiv of **1** in CH_2Cl_2 yields bixanthenyl[33] (**15**) and xanthone[34] (**16**), in 18% and 33% yield, respectively, after 2 d at room temperature (Table 3, entry 7). Similarly, oxidation of **14** with 2 equiv of **2** in CH_2Cl_2 yields **15** and **16**, in 51% and 4% yield, respectively, after 3 d at room temperature (Table 3, entry 7). The presence of bixanthenyl in each reaction mixture can be rationalized by invoking the formation of the xanthenyl radical, which subsequently dimerizes to give the final product. Importantly, its presence provides evidence for an initial one-electron CPET event upon oxidation of xanthene.[35] The presence of xanthone in the reaction mixture can be similarly rationalized. However, instead of coupling to another xanthenyl radical, the xanthenyl radical instead reacts with TEMPO, forming the C−O bond. This TEMPO-xanthenyl intermediate then forms xanthone by release of the piperidyl radical.[29] The reactivity of complexes **1** and **2** with fluorene (**17**) and triphenylmethane (**18**), substrates with slightly stronger C−H bonds than xanthene, was also examined (Table 3, entries 8 and 9). However, no reaction was observed upon addition of 1 equiv of **1** or **2** to either substrate in CD_2Cl_2, even after prolonged reaction times (4 d). Finally, a control reaction between TEMPO and 1,4-cyclohexadiene reveals some reactivity. However, the reaction is extremely slow, only reaching 22% conversion after 4 d at room temperature. Similarly, TEMPO will react with xanthene in the absence of a Lewis acid, but the reaction is slow, only achieving 9% conversion after 4 d. In line with this observations, Gunnoe and co-workers reported that TEMPO will oxidize 1,4-cyclohexadiene at elevated temperatures.[36]

The experiments outlined in Table 3 reveal a clear correlation between the BDE (or BDFE) of the cleaved C−H bond in the substrate and its ability to react with **1** and **2**. The strongest C−H bonds that **1** and **2** are able to activate appear to be those of xanthene (BDE = 77.9 kcal/mol in DMSO) and 9,10-dihydroanthracene (BDE = 80.6 kcal/mol in DMSO),[14,27] which we tested in an earlier study. For comparison, other TEMPO/Lewis acid systems appear to be more reactive. For example, the TEMPO/$Co(OAc)_2$/NaOCl system is capable of

Table 3. Oxidation of Activated Alkanes, Cyclobutanol, and Cyclopropylcarbinol by Complexes 1 and 2

Entry	Substrate	% Conversion Fe	% Conversion Al	Product	% Yield[b] Fe	% Yield[b] Al	BDE[a] (kcal/mol)	BDFE[a] (kcal/mol)
6	 **12**	99	100	 **13**	82	96	76.0	67.8
7	 **14**	100	99	 **15**	18	51	77.9	73.3
				 **16**	33	4		
8	 **17**	0	0	-	N.R.	N.R.	82.0	77.4
9	 **18**	0	0	-	N.R.	N.R.	83.4	78.8
[c]10	 **19**	100	100	 **20**	75	100	-	-
[d]11	 **21**	100	100	 **22**	84	91	-	-
[e]12	 **21**	100	100	 **22**	98	95	-	-

[a]BDE and BDFE from ref 27. [b]Yields determined by ^{1}H NMR spectroscopy. [c]Concentrations of **1** and **2** were 385 and 200 mM, respectively. [d]Concentrations of **1** and **2** were 260 and 190 mM, respectively. [e]Concentrations of **1** and **2** were 6.3 mM and 4.4 mM, respectively.

oxidizing a variety of benzylic C−H bonds, including those of toluene (BDE = 92 kcal/mol in DMSO).[27,37] While the mechanism in the $Co(OAc)_2$ system is not entirely clear, it is possible that these oxidations proceed via the formation of a $[TEMPO]^+$ intermediate and not a TEMPO−Lewis acid adduct, as is likely the case for our system.

Finally, the reactions of complexes **1** and **2** with cyclobutanol (**19**) and cyclopropylcarbinol (**21**) were investigated. Both reagents are common mechanistic probes used to distinguish between oxidations that proceed in one- or two-electron redox steps.[38,39] This discrimination is possible because one-electron oxidants favor the formation of ring-opened products, such as butyraldehyde, or 2- and 3-butenaldehyde, while two-electron oxidants convert **19** and **21** into cyclobutanone (**20**) and cyclopropanecarboxaldehyde (**22**), respectively.[39−42] All the available evidence suggests that complexes **1** and **2** react via an initial 1-electron CPET step. Accordingly, we hypothesized that reaction of complexes **1** or **2** with **19** and **21** would result in formation of ring-opened products. Thus, addition of **19** to 2 equiv of **1** or **2** in C_6D_6 results in complete consumption of the alcohol within 10 min at room temperature, according to ^{1}H NMR spectroscopy. Surprisingly, the only oxidation product observed in the reaction mixture is the ring-closed product **20** (Table 3, entry 10). The reactions of **21** with 2 equiv of **1** or **2** in CD_2Cl_2 also yielded the ring-closed product, **22**, as the only oxidation product (100% conversion; 84 and 91% yield, respectively; Table 3, entry 11). Performing the oxidation of **21** at lower concentrations also only resulted in formation of the ring-closed product, **22** (Table 3, entry 12). These observations are puzzling for several reasons. For one, complex **2** does not contain a redox-active metal center and should only be capable of a one-electron oxidation. Second, this selectivity is at odds with the reactivity observed for the other substrates investigated in this study, such as 2-phenoxyacetophenone (**6**) and xanthene (**14**). These data suggest that multiple pathways could be operative upon reaction of substrate with $MCl_3(\eta^1\text{-TEMPO})$,

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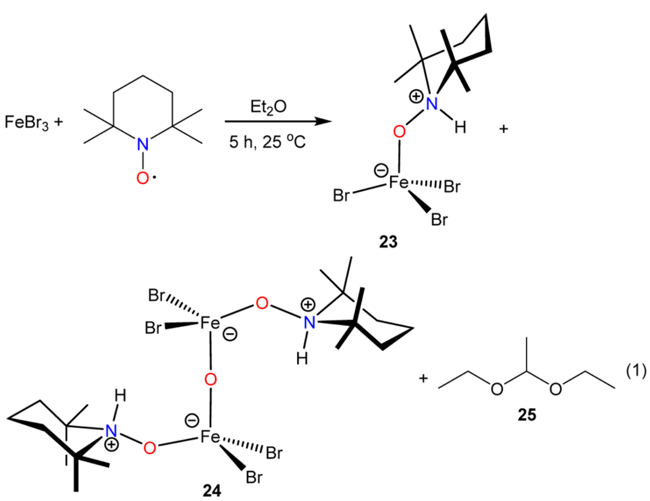
including a two-electron pathway involving the intermediacy of $[TEMPO]^+$ (which can function as a $2e^-$ oxidant). In this regard, we have recently demonstrated that coordination of TEMPO to BBr_3 can generate $[TEMPO]^+$ via disproportionation of the neutral TEMPO radical.[43] In addition, $[TEMPO]^+$ is known to oxidize substituted cyclobutanols to cyclobutanone, without the formation of ring-opened products.[44] Alternately, it is possible that the ring-opening rate constants for cyclobutanol and cyclopropylcarbinol are not large enough to allow for the discrimination between the $1e^-$ and $2e^-$ oxidation pathways in our system. In support of this suggestion, we note that the oxidation of cyclobutanol by $Fe(aq)^{2+}/O_3$ results in the formation of both ring-closed and ring-opened products, demonstrating that the rates of oxidation and ring-opening are comparable in magnitude.[45] Therefore, it is apparent that care must be taken in interpreting results derived from radical clock experiments, and on balance, we still suggest that for our system the $1e^-$ mechanism is most consistent with available evidence.

Activation of TEMPO with $FeBr_3$. Previously, we speculated that activation of TEMPO with stronger Lewis acids would allow us to expand the substrate scope to unactivated alkanes.[14,43] To test this hypothesis we explored the reaction of $FeBr_3$ with TEMPO. While a quantitative evaluation of the Lewis acidity of $FeBr_3$ has not been performed,[46] it is likely to be a stronger Lewis acid than $FeCl_3$. We based this conclusion on the knowledge that bromide salts are often better Lewis acids that their chloride congeners. For example, it is well-established that BBr_3 is a stronger Lewis acid that BCl_3.[47−49] Likewise, thermochemical data suggest that $AlBr_3$ is a stronger Lewis acid than $AlCl_3$.[46] Given these considerations, we rationalized that $FeBr_3$ would likely follow the same trend as the group 13 Lewis acids. Accordingly, addition of 1 equiv of TEMPO to an Et_2O solution of $FeBr_3$ results in the immediate formation of an orange precipitate. A subsequent ^1H NMR analysis of this solid reveals the presence of two major species, identified as $FeBr_3(\eta^1$-TEMPOH) (**23**) and $[FeBr_2(\eta^1\text{-TEMPOH})]_2(\mu\text{-O})$ (**24**) (eq 1). These species are present in an approximate 3:2 ratio, respectively.



The identity of complex **23** was determined by comparison of its ^1H NMR spectral parameters with those of its chloride congener, $FeCl_3(\eta^1$-TEMPOH).[14] In particular, **23** features a diagnostic resonance at δ 59.20 ppm, assignable to a TEMPO β-H resonance, in its ^1H NMR spectrum in CD_2Cl_2 (Supporting Information Figure S31). This chemical shift is nearly identical to the analogous TEMPO β-H resonance observed for $FeCl_3(\eta^1$-TEMPOH).[14] Unfortunately, we have been unable to cleanly separate complex **23** from **24**, and so are unable to complete its characterization. However, we have been able to isolate a few X-ray quality crystals of **23**, which has permitted its characterization by X-ray crystallography. Complex **23** crystallizes in the orthorhombic space group *Pnma*, and its solid state molecular structure is shown in Figure 1. Complex **23** is isostructural with

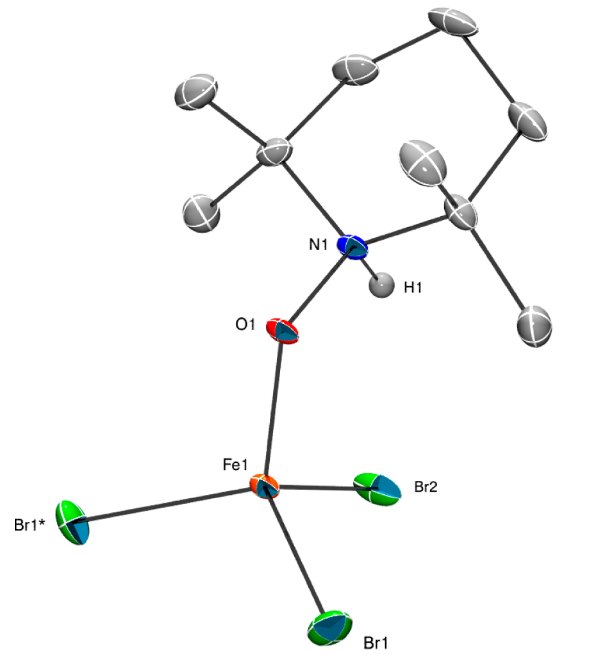


Figure 1. ORTEP diagram of $FeBr_3(\eta^1$-TEMPOH) (**23**) with 50% probability ellipsoids. All hydrogen atoms, except the N−H hydrogen atom, are omitted for clarity. Atoms labeled with an asterisk are generated by symmetry. Selected bond lengths (Å) and angles (deg): Fe1−Br1 = 2.3184(3) Å, Fe1−Br2 = 2.3396(5) Å, Fe1−O1 = 1.882(2) Å, N1−O1 = 1.406(3) Å, $\sum$(E−N1−E) = 339.2°.

$MCl_3(\eta^1$-TEMPOH) (M = Fe, Al).[14] It features an N1−O1 bond length of 1.406(3) Å, consistent with the presence of the reduced $[TEMPO]^-$ moiety. In addition, the sum of the angles around N1 is 339.2°, while a hydrogen atom was located in the difference map and successfully refined on N1. Finally, the Fe1−O1 bond length in **23** is 1.882(2) Å, which is similar to that exhibited by $FeCl_3(\eta^1$-TEMPOH).[14] Interestingly, addition of 1 equiv of TEMPOH to an Et_2O solution of $FeBr_3$ also generates a mixture of **23** and **24**. Under these conditions, **23** and **24** are formed in a 1:1 ratio, according to ^1H NMR spectroscopy (Supporting Information Figure S32).

Complex **24** can be generated in higher yield by reaction of 1 equiv of TEMPO with $FeBr_3$ in Et_2O, in the presence of 1 equiv of 1,4-cyclohexadiene. When formed in this manner, it can then be separated from the small amount of **23** that is also generated in the reaction by recrystallization twice from CH_2Cl_2/Et_2O. Generated in this fashion, **24** can be isolated as an orange crystalline solid in 32% yield. Its ^1H NMR spectrum in CD_2Cl_2 exhibits two broad resonances at δ 3.72 and 1.86 ppm, assignable to the methyl protons of TEMPOH, and three broad resonances at δ 6.39, 2.36, and 1.64 ppm, assignable to the methylene protons of TEMPOH. The resonance assignable to the NH proton is observed at δ 47.21 ppm. We suggest that the bridged oxo ligand in complex **24** is derived from the TEMPO moiety,

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based on the well-established ability of TEMPO to act as an oxygen atom source in both transition metal and actinide systems.[29,50−53] For example, reaction of $Fe(hfac)_2(H_2O)_2$ with TEMPO results in O atom transfer and formation of an Fe(III) oxo-bridged dimer, along with formation of the piperidinium ion.[54]

Complex **24** crystallizes in the orthorhombic space group *Pccn*, and its solid state molecular structure is shown in Figure 2. In the solid state, complex **24** exists as a bimetallic oxo-bridged complex. The Fe−O(oxo) bond length in **24** is 1.7702(7) Å, which is consistent with the presence of a Fe(III)-bridged oxo linkage. For comparison, the closely related Fe(III) complex, $[FeBr_2(HNP(^tBu)_3)]_2(\mu\text{-}O)$, features Fe−O(oxo) bond lengths of 1.768(7) and 1.760(7) Å.[55] The Fe−O(TEMPOH) bond length in **24** (Fe1−O2 = 1.889(2) Å) is comparable to that of **1** (Fe−O = 1.8996(12) Å),[14] while the metrical parameters of the TEMPOH ligand in **24** are consistent with the presence of $[TEMPO]^-$, indicating that reduction of this moiety has occurred.[14,56] In particular, the N1−O2 bond length in **24** is 1.396(3) Å, while the sum of the angles around N1 is 330.0°. Additionally, a hydrogen atom was located in the difference map and successfully refined on N1. Finally, the Fe−Br bond lengths in **24** (av 2.34 Å) are consistent with those of **23** and other Fe^{3+} bromide complexes.[55]

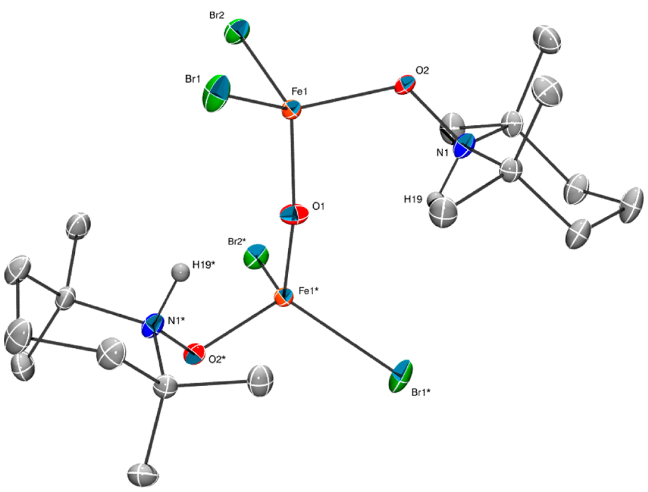

Figure 2. ORTEP diagram of $[FeBr_2(\eta^1\text{-TEMPOH})]_2(\mu\text{-}O)$ (**24**) with 50% probability ellipsoids. All hydrogen atoms, except the N−H hydrogen atom, are omitted for clarity. Atoms labeled with an asterisk are generated by symmetry. Selected bond lengths (Å) and angles (deg): Fe1−Br1 = 2.3565(4) Å, Fe1−Br2 = 2.3312(5) Å, Fe1−O1 = 1.7702(7) Å, Fe1−O2 = 1.889(2) Å, N1−O2 = 1.396(3) Å, $\sum$(E−N1−E) = 330.0°.

We have also attempted to identify the organic products formed during the formation of **23** and **24**. Thus, the supernatant formed upon addition of 1 equiv of TEMPO to an Et_2O solution of $FeBr_3$ was filtered through basic alumina to remove the metal containing products. A GC/MS trace of the resulting filtrate reveals the presence of 1,1-diethoxyethane (**25**) (Supporting Information Figure S41). Its formation can be rationalized by invoking the formation of an Et_2O methylene radical, which subsequently reacts with a molecule of Et_2O, resulting in C−O bond cleavage, formation of 1,1-diethoxyethane, and ejection of an ethyl radical. It is unlikely that **25** is the only oxidation product generated in the reaction; however, other possible Et_2O oxidation products, such as acetaldehyde,[57−59] ethylene, or ethane, were not observed in the GC trace, likely because of their greater volatility versus that of Et_2O. Ethanol, another possible oxidation product,[57] was also not observed. Interestingly, however, unreacted TEMPO was observed in the GC/MS trace. The GC/MS analysis is significant because it confirms that $FeBr_3$/TEMPO can oxidize the methylene C−H bond in Et_2O, which is a stronger C−H bond (BDE = 92.5 kcal/mol) than the other substrates that we have probed.[27,60]

■ CONCLUSIONS

In summary, we have shown that the Lewis acid-TEMPO adducts, $MCl_3(\eta^1\text{-TEMPO})$ (M = Fe, **1**; Al, **2**), can oxidize the lignin models 3,4-dimethoxybenzyl alcohol (**3**), 1-phenyl-2-phenoxyethanol (**5**), and 1,2-diphenyl-2-methoxyethanol (**8**) at room temperature. While these simple molecules are not very accurate models of lignin, they nonetheless represent a good starting point for further studies with lignin itself. Their oxidations likely proceed via an initial 1-electron CPET event, a hypothesis that is supported by the isolation of 2-(2,2,6,6-tetramethylpiperidyl-*N*-oxyl)-2-phenoxyacetophenone (**7**) upon oxidation of either **5** or 2-phenoxyacetophenone (**6**) by complex **2**. The isolation of bixanthenyl (**15**) upon oxidation of xanthene (**14**) by complexes **1** or **2** also supports this premise. The reaction of TEMPO with $FeBr_3$ in Et_2O results in the formation of a mixture of $FeBr_3(\eta^1\text{-TEMPOH})$ and $[FeBr_2(\eta^1\text{-TEMPOH})]_2(\mu\text{-}O)$, via oxidation of the solvent, Et_2O. This result further confirms the hypothesis that the strength of the Lewis acid can modulate the oxidation potential of TEMPO and result in an expanded substrate scope. We will continue to probe the reactivity of TEMPO with Lewis acids of varying strengths to further our understanding of the mechanisms of TEMPO-mediated oxidations, and search for *N*-oxyl radicals that are less sensitive to N−O bond cleavage.

■ EXPERIMENTAL SECTION

General Procedures. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions under an atmosphere of nitrogen. Hexanes, diethyl ether, and toluene were dried by passage over activated molecular sieves using a Vacuum Atmospheres solvent purification system, while C_6D_6, CD_2Cl_2, and toluene-d_8 were dried over 3 Å molecular sieves for 24 h prior to use. Methylene chloride, mesitylene, 3,4-dimethoxybenzyl alcohol (**3**), cyclobutanol (**19**), and cyclopropylcarbinol (**21**) were degassed and dried over 3 Å molecular sieves for 24 h prior to use. $AlCl_3(\eta^1\text{-TEMPO})$ (**2**),[14] $FeCl_3(\eta^1\text{-TEMPO})$ (**1**),[14] 1-phenyl-2-phenoxyethanol (**5**),[61] 2-phenoxyacetophenone (**6**),[62] 1,2-diphenyl-2-methoxyethanol (**8**) (mixture of 85:15 u (*R*,*S* + *S*,*R*):l (*R*,*R* + *S*,*S*) diastereomers),[21] and anhydrous TEMPOH[63] were prepared according to the previously reported procedures. NMR spectral data for these compounds were consistent with those reported in the literature (note that the ^1H NMR spectral data for TEMPOH in C_6D_6 differ substantially between refs 63 and 64; our data were consistent with those in ref 64).[14,61,38,64] Compound **8** was recrystallized from a concentrated CH_2Cl_2 solution at −25 °C and washed with cold Et_2O (3 × 1 mL) before use. All other reagents were purchased from commercial suppliers and used as received.

All NMR spectra were collected at 25 °C. ^1H NMR spectra were recorded on a Varian UNITY INOVA 400 MHz spectrometer, an Agilent Technologies 400-MR DD2 400 MHz spectrometer, a Varian UNITY INOVA 500 MHz spectrometer, or an actively shielded Varian UNITY INOVA 600 MHz spectrometer. $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian UNITY INOVA 500 MHz spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra are referenced to external $SiMe_4$ using the residual protio solvent peaks as internal standards (^1H NMR experiments) or the characteristic resonances of the solvent nuclei ($^{13}C\{^1H\}$ NMR experiments). All ^1H NMR spectra containing mesitylene as an internal standard were recorded with a relaxation delay time (d1) of 60 s. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer with a NXR FT Raman Module. GC/MS traces were collected on a Hewlett-Packard 5890A GC coupled to a Hewlett-Packard 5970B Mass Selective Detector (MSD), equipped with a J&W DB-5 ms capillary column (30 m × 0.25 mm i.d. with 0.25 μm film thickness). The MSD has a dedicated electron ionization (EI) source and a quadrupole mass analyzer. All other mass spectra were collected by the Mass Spectrometry Facility at the University of California, Santa Barbara. Elemental analyses were performed by the Micro-Mass Facility at the University of California, Berkeley.

Synthesis of 2-Methoxy-1,2-diphenylethanone (9). 2-Methoxy-1,2-diphenylethanone was prepared according to a previously reported procedure[65] for using Dess-Martin periodinane (DMP) to oxidize alcohols: To a stirring CH_2Cl_2 (3 mL) solution of 1,2-diphenyl-2-methoxyethanol (149.8 mg, 656.2 μmol) was added dropwise a CH_2Cl_2 (10 mL) solution of DMP (337.5 mg, 795.7 μmol). The reaction mixture was allowed to stir for 2.5 h, whereupon it was transferred to a separatory funnel containing 5% NaOH (aq) (10 mL) and Et_2O (20 mL). The organic layer was separated and rinsed with H_2O (2 × 30 mL), dried with anhydrous $MgSO_4$, and filtered to give a colorless solution. The solvent was then removed in vacuo to provide a white solid that was recrystallized from a concentrated CH_2Cl_2/Et_2O (1:1) solution at −25 °C and washed with cold Et_2O (3 × 1 mL): 133.2 mg, 90% yield of **9**. ^{1}H NMR (500 MHz, 25 °C, CD_2Cl_2): δ 3.43 (s, 3H, OC*H*$_3$), 5.52 (s, 1 H, C*H*), 7.30 (m, 1H, *p*-Ph), 7.35 (m, 2H, *m*-Ph), 7.39−7.45 (m, 4H, Ph), 7.53 (m, 1H, *p*-Ph), 7.97 (m, 2H, *o*-Ph). ^{13}C{^{1}H} NMR (126 MHz, 25 °C, CD_2Cl_2): δ 57.91 (CH_3), 87.00 (HCOMe), 128.21 (Ar), 129.01 (Ar), 129.04 (Ar), 129.31 (Ar), 129.44 (Ar), 133.75 (Ar), 135.78 (Ar), 136.95 (Ar), 197.46 (CO). FI-MS: *m/z* 226.10 $[M]^+$, 121.08 $[C_6H_5CHOCH_3$ fragment$]^+$, 105.04 $[C_6H_5CO$ fragment$]^+$.

Oxidation of 3,4-Dimethoxybenzyl Alcohol by $FeCl_3(\eta^1$-TEMPO). 3,4-Dimethoxybenzyl alcohol (5 μL, 34.4 μmol) was added via microsyringe to a stirring Et_2O solution (2 mL) of $FeCl_3(\eta^1$-TEMPO) (23.9 mg, 75.1 μmol). The purple solution immediately lightened upon addition of the alcohol, concomitant with the deposition of a reddish tan precipitate. The reaction mixture was allowed to stir for 10 min, whereupon it was filtered through a basic alumina column (1 cm × 0.5 cm) supported on glass wool. The column was subsequently rinsed with Et_2O (5 mL) to provide a colorless filtrate. The solvent was removed in vacuo, and the resulting residue was dissolved in C_6D_6 (700 μL) and transferred to an NMR tube. Mesitylene (5 μL, 35.9 μmol) was added via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed complete consumption of the alcohol and formation of 3,4-dimethoxybenzaldehyde in 75% yield. NMR spectral data of the product are consistent with those reported in the literature for 3,4-dimethoxybenzaldehyde.[10] ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ 3.21 (s, 3H, OC*H*$_3$), 3.25 (s, 3H, OC*H*$_3$), 6.34 (d, *J* = 8.1 Hz, 1H, Ph), 7.08 (dd, *J* = 8.1, 1.9 Hz, 1H, Ph), 7.35 (d, *J* = 1.9 Hz, 1H, Ph), 9.75 (s, 1H, C*H*O).

Oxidation of 3,4-Dimethoxybenzyl Alcohol by $AlCl_3(\eta^1$-TEMPO). $AlCl_3(\eta^1$-TEMPO) (26.3 mg, 90.8 μmol) was dissolved in CD_2Cl_2 (700 μL) and transferred to an NMR tube. 3,4-Dimethoxybenzyl alcohol (5 μL, 34.4 μmol) was then added via microsyringe. Within 3 min, the clear yellow solution lightened to a very faint yellow. After 2 h, mesitylene (5 μL, 35.9 μmol) was added via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed complete consumption of the alcohol and formation of 3,4-dimethoxybenzaldehyde in 99% yield. NMR spectral data of the product are consistent with those reported in the literature for 3,4-dimethoxybenzaldehyde.[10] ^{1}H NMR (600 MHz, 25 °C, CD_2Cl_2): 3,4-dimethoxybenzaldehyde: δ 3.90 (s, 3H, OC*H*$_3$), 3.93 (s, 3H, OC*H*$_3$), 7.01 (d, *J* = 8.2 Hz, 1H, Ph), 7.39 (s, 1H, Ph), 7.48 (d, *J* = 7.9 Hz, 1H, Ph), 9.83 (s, 1H, C*H*O). $AlCl_3(\eta^1$-TEMPOH): δ 1.43 (s, 6H, C*H*$_3$), 1.55 (s, 6H, C*H*$_3$), 1.63−1.85 (m, 4H, C*H*$_2$), 1.99 (d, *J* = 14.5 Hz, 2H, C*H*$_2$), 7.15 (br s, 1H, N-*H*).

Oxidation of 1-Phenyl-2-phenoxyethanol by $FeCl_3(\eta^1$-TEMPO). An Et_2O solution (1.5 mL) of $FeCl_3(\eta^1$-TEMPO) (18.9 mg, 59.3 μmol) was added to a stirring Et_2O solution (0.5 mL) of 1-phenyl-2-phenoxyethanol (5.2 mg, 24.3 μmol), resulting in the immediate conversion of the deep purple solution to a red-brown suspension. The reaction mixture was allowed to stir for 18 h, whereupon it was filtered through a basic alumina column (1.5 cm × 0.5 cm) supported on glass wool. The column was then rinsed with Et_2O (6 mL) to provide a colorless filtrate. The solvent was removed in vacuo, and the resulting white solid was dissolved in CD_2Cl_2 (700 μL). This solution was transferred to an NMR tube, mesitylene (5 μL, 35.9 μmol) was added via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed complete consumption of the alcohol and formation of 2-phenoxyacetophenone in 65% yield. This was confirmed by comparison of the NMR spectral data to that of an authentic sample of 2-phenoxyacetophenone.[61] ^{1}H NMR (600 MHz, 25 °C, CD_2Cl_2): δ 5.32 (s, 2H, C*H*$_2$), 6.94 (d, *J* = 8.2 Hz, 2H, *o*-Ph), 7.00 (t, *J* = 7.4 Hz, 1H, *p*-Ph), 7.31 (t, *J* = 7.8 Hz, 2H, *m*-Ph), 7.54 (t, *J* = 7.7 Hz, 2H, *m*-Ph), 7.65 (t, *J* = 7.5 Hz, 1H, *p*-Ph), 8.01 (d, *J* = 7.6 Hz, 2H, *o*-Ph).

Oxidation of 1-Phenyl-2-phenoxyethanol by $AlCl_3(\eta^1$-TEMPO). $AlCl_3(\eta^1$-TEMPO) (15.1 mg, 52.1 μmol) was added to a solution of 1-phenyl-2-phenoxyethanol (5.0 mg, 23.3 μmol) dissolved in CH_2Cl_2 (1 mL). The yellow solution was allowed to stand without stirring for 3 h. The color of the solution gradually lightened over this time. The solvent was removed in vacuo, and the resulting solid was extracted into Et_2O (3 mL) and filtered through a basic alumina column (1.5 cm × 0.5 cm) supported on glass wool. The column was then rinsed with Et_2O (6 mL) to provide a colorless filtrate. The solvent was removed in vacuo, and the resulting white solid was dissolved in CD_2Cl_2 (700 μL). This solution was transferred to an NMR tube, mesitylene (5 μL, 35.9 μmol) was added via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed complete consumption of 1-phenyl-2-phenoxyethanol, and formation of 2-phenoxyacetophenone (**6**) and 2-(2,2,6,6-tetramethylpiperidine-*N*-oxyl)-2-phenoxyacetophenone (**7**) in 75% yield and 5% yield, respectively. The identities of these products were confirmed by comparison of the NMR spectral data to that of authentic material. ^{1}H NMR (500 MHz, 25 °C, CD_2Cl_2): for **6**, δ 5.31 (s, 2H, C*H*$_2$), 6.93 (d, *J* = 8.8 Hz, 2H, *o*-Ph), 6.99 (t, *J* = 6.9 Hz, 1H, *p*-Ph), 7.30 (m, 2H, *m*-Ph), 7.53 (t, *J* = 7.8 Hz, 2H, *m*-Ph), 7.65 (t, *J* = 7.4 Hz, 1H, *p*-Ph), 7.99 (d, *J* = 8.0 Hz, 2H, *o*-Ph); for **7**, δ 1.03 (s, 3H, C*H*$_3$), 1.23 (s, 3H, C*H*$_3$), 1.36 (s, 3H, C*H*$_3$), 6.02 (s, 1H, C*H*), 8.26 (d, *J* = 7.98 Hz, 2H, *o*-Ph), missing methyl resonance overlaps with solvent, missing aryl resonances overlap with those of compound **6**.

Oxidation of 2-Phenoxyacetophenone by $FeCl_3(\eta^1$-TEMPO). An Et_2O solution (1.5 mL) of $FeCl_3(\eta^1$-TEMPO) (49.2 mg, 154.5 μmol) was added to a stirring Et_2O solution (0.5 mL) of 2-phenoxyacetophenone (15.1 mg, 71.1 μmol). The reaction mixture was allowed to stir for 18 h, whereupon a small amount of dark solid precipitated. The solution remained dark purple. This reaction mixture was filtered through a basic alumina column (2 cm × 0.5 cm) supported on glass wool. The column was then rinsed with Et_2O (6 mL) to provide a pale orange filtrate. The solvent was removed in vacuo, and the resulting pale orange solid was dissolved in CD_2Cl_2 (700 μL). This solution was transferred to an NMR tube, mesitylene (5 μL, 35.9 μmol) was added via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed the formation of **7** (3% yield) and the presence of unreacted 2-phenoxyacetophenone (73% yield). ^{1}H NMR (600 MHz, 25 °C, CD_2Cl_2): for **6**, δ 5.32 (s, 2H, C*H*$_2$), 6.95 (d, *J* = 7.63 Hz, 2H, *o*-Ph), 7.01 (t, *J* = 6.86 Hz, 1H, *p*-Ph), 7.32 (t, *J* = 7.12 Hz, 2H, *m*-Ph), 7.54 (t, *J* = 7.03 Hz, 2H, *m*-Ph), 7.66 (t, *J* = 6.74 Hz, 1H, *p*-Ph), 8.01 (d, *J* = 7.2 Hz, 2H, *o*-Ph); for **7**, δ 1.05 (s, 3H, C*H*$_3$), 1.25 (s, 3H, C*H*$_3$), 1.38 (s, 3H, C*H*$_3$), 6.04 (s, 1H, C*H*), 8.28 (d, *J* = 7.45 Hz, 2H, *o*-Ph), missing aryl resonances overlap with those of compound **6**, and unassigned CH_2 and CH_3 resonances of **7** overlap with C*H*$_3$ resonances and solvent.

Oxidation of 2-Phenoxyacetophenone by $AlCl_3(\eta^1$-TEMPO). $AlCl_3(\eta^1$-TEMPO) (22.7 mg, 78.4 μmol) was added to a solution of 2-

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phenoxyacetophenone (7.0 mg, 33.0 μmol) dissolved in CH_2Cl_2 (1 mL). The yellow solution was allowed to stand without stirring for 3 h. The solvent was removed in vacuo, and the resulting solid was extracted into Et_2O (4 mL) and filtered through a basic alumina column (1.5 cm × 0.5 cm) supported on glass wool. The column was then rinsed with Et_2O (6 mL) to provide a colorless filtrate. The solvent was removed in vacuo, and the resulting colorless oil was dissolved in CD_2Cl_2 (700 μL). This solution was transferred to an NMR tube, mesitylene (5 μL, 35.9 μmol) was added via microsyringe, and ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed the formation of **7** in 48% yield and the presence of unreacted 2-phenoxyacetophenone in 4% yield. For compound **7**, ^{1}H NMR (400 MHz, 25 °C, CD_2Cl_2): δ 1.02 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.32 (s, 2H, γ-CH_2 overlapping with CH_3 resonance), 1.36 (s, 3H, CH_3), 1.43−1.67 (m, 4H, β-CH_2 overlapping with solvent), 6.01 (s, 1H, C*H*), 6.95−7.05 (m, 3H, Ph), 7.25 (t, *J* = 8.0 Hz, 2H, *m*-Ph), 7.50 (t, *J* = 7.6 Hz, 2H, *m*-Ph), 7.60 (t, *J* = 7.4 Hz, 1H, *p*-Ph), 8.26 (d, *J* = 7.9 Hz, 2H, *o*-Ph). ^{13}C{^{1}H} NMR (126 MHz, 25 °C, CD_2Cl_2): δ 17.62 (γ-CH_2), 20.46 (CH_3), 21.19 (CH_3), 33.41 (CH_3), 34.14 (CH_3), 40.35 (β-CH_2), 40.73 (β-CH_2), 60.54 (α-C), 61.71 (α-C), 110.35 (CHO), 117.31 (*o*-CH), 122.70 (*p*-CH), 128.85 (*m*-CH), 130.02 (*m*-CH), 130.86 (*o*-CH), 133.69 (*i*-C), 134.06 (*p*-CH), 157.30 (*i*-C), 192.98 (CO). ESI-MS: *m/z* 390.21 [M + Na]$^+$, 757.44 [2 M + Na]$^+$.

Oxidation of 1,2-Diphenyl-2-methoxyethanol by FeCl$_3$(η^1-TEMPO). A CH_2Cl_2 (0.5 mL) solution of $FeCl_3$(η^1-TEMPO) (23.7 mg, 74.4 μmol) was added to a CH_2Cl_2 (0.5 mL) solution of 1,2-diphenyl-2-methoxyethanol (6.4 mg, 28.0 μmol). The deep purple solution immediately lightened to maroon. This solution was allowed to stand without stirring for 2 h. The reaction mixture was filtered through a basic alumina column (2 cm × 0.5 cm) supported on glass wool. The column was then rinsed with Et_2O (6 mL) to provide a pale orange filtrate. The solvent was removed in vacuo, and the resulting light orange oil was dissolved in CD_2Cl_2 (700 μL). This solution was transferred to an NMR tube, mesitylene (5 μL, 35.9 μmol) was added via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed complete consumption of the alcohol and formation of 2-methoxy-1,2-diphenylethanone in 75% yield. The identity of this product was confirmed by comparison of the NMR spectral data to that of authentic material.[10] ^{1}H NMR (600 MHz, 25 °C, CD_2Cl_2): δ 3.43 (s, 3H, CH_3), 5.52 (s, 1H, C*H*), 7.31 (t, *J* = 7.3 Hz, 1H, Ph), 7.36 (t, *J* = 7.4 Hz, 2H, Ph), 7.39−7.45 (m, 4H, Ph), 7.53 (t, *J* = 7.4 Hz, 1H, Ph), 7.97 (d, *J* = 7.4 Hz, 2H, Ph). FI-MS: *m/z* 226.10 [M]$^+$, 121.08 [$C_6H_5CHOCH_3$ fragment]$^+$, 105.04 [C_6H_5CO fragment]$^+$.

Oxidation of 1,2-Diphenyl-2-methoxyethanol by AlCl$_3$(η^1-TEMPO). $AlCl_3$(η^1-TEMPO) (58.6 mg, 202.4 μmol) was added to a CH_2Cl_2 (1 mL) solution of 1,2-diphenyl-2-methoxyethanol (22.0 mg, 96.4 μmol). This orange reaction mixture was allowed to stand without stirring for 3 h. The solvent was then removed in vacuo, and the resulting solid was extracted into Et_2O (3 mL) and filtered through a basic alumina column (2 cm × 0.5 cm) supported on glass wool. The column was rinsed with Et_2O (6 mL) to provide a pale yellow filtrate. The solvent was removed in vacuo, and the resulting light yellow oil was dissolved in CD_2Cl_2 (700 μL). This solution was transferred to an NMR tube, mesitylene (5 μL, 35.9 μmol) was added via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed the presence of unreacted 1,2-diphenyl-2-methoxyethanol (**8**) in 23% yield, the formation of benzil (**10**) in 54% yield (based on **2**), and the formation of a minor unidentified product, as evidenced by a methoxy resonance at 3.51 ppm. The identity of benzil was confirmed by comparison of the NMR spectral data to that of authentic material.[66] ^{1}H NMR (600 MHz, 25 °C, CD_2Cl_2): δ 3.21 (s, 3H, OCH_3, **8**), 3.51 (s, 3H, OCH_3, unknown minor product), 4.35 (s, 1H, C*H*, **8**), 4.88 (s, 1H, C*H*, **8**), 7.14−7.32 (m, Ar, **8**, overlapping with unknown minor product), 7.55 (t, *J* = 7.83 Hz, 4H, *m*-Ph, **10**, overlapping with unknown minor product), 7.70 (t, *J* = 7.1 Hz, 2H, *p*-Ph, **10**), 7.97 (d, *J* = 8.22 Hz, 4H, *o*-Ph, **10**, overlapping with unknown minor product). ESI-MS: *m/z* 251.11 [**8** + Na]$^+$. FI-MS: *m/z* 228.11 [**8**]$^+$, 210.07 [**10**]$^+$.

Attempted Oxidation of 2-Methoxy-1,2-diphenylethanone by FeCl$_3$(η^1-TEMPO). $FeCl_3$(η^1-TEMPO) (22.8 mg, 71.6 μmol) was added to a solution of 2-methoxy-1,2-diphenylethanone (7.1 mg, 31.4 μmol) dissolved in CH_2Cl_2 (1 mL). This dark purple reaction mixture was allowed to stand without stirring for 15 h. No color change or formation of precipitate was observed over this time frame. Et_2O (2 mL) was added to the reaction mixture. This solution was then filtered through a basic alumina column (2 cm × 0.5 cm) supported on glass wool and rinsed with Et_2O (10 mL) to provide a pale orange filtrate. The solvent was removed in vacuo, and the resulting oil was dissolved in CD_2Cl_2 (700 μL). This solution was transferred to an NMR tube, mesitylene (5 μL, 35.9 μmol) was added via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed a 98% recovery of the starting 2-methoxy-1,2-diphenylethanone and no formation of oxidation products.

Oxidation of 2-Methoxy-1,2-diphenylethanone by AlCl$_3$(η^1-TEMPO). $AlCl_3$(η^1-TEMPO) (32.6 mg, 112.6 μmol) was added to a solution of 2-methoxy-1,2-diphenylethanone (11.4 mg, 50.4 μmol) dissolved in CH_2Cl_2 (1 mL). The dark yellow reaction mixture was allowed to stand without stirring for 15 h, whereupon the solvent was removed in vacuo. The resulting solid was extracted into Et_2O (3 mL) and filtered through a basic alumina column (2 cm × 0.5 cm) supported on glass wool. The column was then rinsed with Et_2O (6 mL) to provide a pale yellow filtrate. The solvent was removed in vacuo, and the resulting solid was dissolved in CD_2Cl_2 (700 μL). This solution was transferred to an NMR tube, mesitylene (5 μL, 35.9 μmol) was added via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed the presence of 2-methoxy-1,2-diphenylethanone (**9**) in 11% yield, and the formation of benzil (**10**) and 2,2-dimethoxy-2-phenylacetophenone (**11**) in 53% and 16% yields, respectively. The identities of the products were confirmed by comparison of the NMR and mass spectral data to those of authentic sample.[66,67] ^{1}H NMR (600 MHz, 25 °C, CD_2Cl_2): δ 3.20 (s, 3H, OCH_3, **11**), 3.44 (s, 3H, OCH_3, **9**), 5.52 (s, 1H, C*H*, **9**), 7.27−7.48 (m, overlapping aryl CH of **9** and **11**), 7.54 (t, *J* = 7.7 Hz, Ar of **10**, overlapping aryl CH of **9**), 7.59 (d, *J* = 7.7 Hz, 2H, *o*-Ph, **11**), 7.69 (t, *J* = 7.5 Hz, 2H, *p*-Ph, **10**), 7.97 (d, *J* = 7.8 Hz, *o*-Ph of **10**, overlapping aryl CH of **9**), 8.04 (d, *J* = 7.9 Hz, 2H, *o*-Ph, **11**). ESI-MS: *m/z* 249.09 [**9** + Na]$^+$, 279.11 [**11** + Na]$^+$. FI-MS: *m/z* 226.10 [**9**]$^+$, 210.07 [**10**]$^+$.

Oxidation of 1,4-Cyclohexadiene by FeCl$_3$(η^1-TEMPO). $FeCl_3$(η^1-TEMPO) (36.4 mg, 114.3 μmol) was dissolved in toluene-d_8 (700 μL), and 1,4-cyclohexadiene (5 μL, 52.9 μmol) was added via microsyringe. The dark purple solution immediately lightened. The reaction was allowed to stand for 2 h without stirring. The solution was then filtered through a basic alumina column (1 cm × 0.5 cm) supported on glass wool into an NMR tube. The column was rinsed with toluene-d_8 (0.5 mL), mesitylene (5 μL, 35.9 μmol) was added to the NMR tube via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed the presence of unreacted 1,4-cyclohexadiene in 1% yield, and formation of benzene in 82% yield. ^{1}H NMR (600 MHz, 25 °C, toluene-d_8): benzene: δ 7.14 (s, 6H, C*H*); 1,4-cyclohexadiene: δ 2.52 (s, 4H, CH_2), 5.59 (s, 4H, C*H*).

Oxidation of 1,4-Cyclohexadiene by AlCl$_3$(η^1-TEMPO). $AlCl_3$(η^1-TEMPO) (35.8 mg, 123.6 μmol) was dissolved in CD_2Cl_2 (700 μL) and transferred to an NMR tube. An initial ^{1}H NMR spectrum was recorded. 1,4-Cyclohexadiene (5 μL, 52.9 μmol) was then added via microsyringe, whereupon the yellow solution immediately lightened. After 15 min, mesitylene (5 μL, 35.9 μmol) was added via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed the complete consumption of 1,4-cyclohexadiene and the formation of benzene in 96% yield. ^{1}H NMR (400 MHz, 25 °C, CD_2Cl_2): benzene, δ 7.36 (s, 6H, C*H*); $AlCl_3$(η^1-TEMPOH), δ 1.43 (s, 6H, CH_3), 1.55 (s, 6H, CH_3), 1.63−1.85 (m, 4H, CH_2), 1.99 (d, *J* = 14.29 Hz, 2H, CH_2), 7.14 (br s, 1H, N-*H*).

Oxidation of Xanthene by $FeCl_3(\eta^1$-TEMPO). $FeCl_3(\eta^1$-TEMPO) (109.6 mg, 344.2 μmol) was added to a CH_2Cl_2 (3 mL) solution of xanthene (28.5 mg, 156.4 μmol). After 48 h, the orange reaction mixture was filtered through a basic alumina column (2.5 cm × 0.5 cm) supported on glass wool, and the column was rinsed with Et_2O (6 mL) to provide a nearly colorless filtrate. The solvent was removed in vacuo, and the resulting white solid was dissolved in CD_2Cl_2 (700 μL). This solution was transferred to an NMR tube, mesitylene (5 μL, 35.9 μmol) was added via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed the absence of xanthene, and formation of bixanthenyl (**15**) and xanthone (**16**) in 18% yield and 33% yield, respectively. The NMR spectral data of the products are consistent with those previously reported for bixanthenyl and xanthone.[33,34] ^{1}H NMR (500 MHz, 25 °C, CD_2Cl_2): for **16**, δ 7.40 (m, 2H, Ar), 7.50−7.54 (m, 2H, Ar), 7.75 (m, 2H, Ar), 8.30 (dd, *J* = 7.9, 1.8 Hz, 2H, Ar); for **15**, δ 4.26 (s, 2H, C*H*), 6.70 (dd, *J* = 7.6, 1.6 Hz, 4H, Ar), 6.83 (dd, *J* = 8.1, 1.2 Hz, 4H, Ar), 6.95 (td, *J* = 7.4, 1.2 Hz, 4H, Ar), 7.21 (m, 4H, Ar). ^{13}C{^{1}H} NMR (126 MHz, 25 °C, CD_2Cl_2): for **16**, δ 118.56 (CH), 122.36 (*C*(C=O)*C*), 124.46 (CH), 126.99 (CH), 135.39 (CH), 156.77 (*C*O*C*), 177.36 (*C*=O); for **15**, δ 49.99 (CH), 116.23 (Ar CH), 122.43 (*C*), 123.23 (Ar CH), 128.63 (Ar CH), 129.74 (Ar CH), 153.56 (*C*O*C*).

Oxidation of Xanthene by $AlCl_3(\eta^1$-TEMPO). $AlCl_3(\eta^1$-TEMPO) (77.3 mg, 266.9 μmol) was added to a CH_2Cl_2 (700 μL) solution of xanthene (24.1 mg, 132.3 μmol) and transferred to a J. Young NMR tube. Mesitylene (5 μL, 35.9 μmol) was added via microsyringe, and the yellow solution was monitored by ^{1}H NMR spectroscopy for 72 h, during which time it gradually darkened to orange. The solvent was removed in vacuo, and the resulting solid was extracted into toluene (2 mL) and filtered through a basic alumina column (1.5 cm × 0.5 cm) supported on glass wool. The column was then rinsed with toluene (6 mL) to provide a colorless filtrate. The solvent was removed in vacuo, and the white solid was dissolved in CD_2Cl_2 (700 μL). This solution was transferred to an NMR tube, mesitylene (5 μL, 35.9 μmol) was added via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed the presence of unreacted xanthene (**14**) in 1% yield, and formation of bixanthenyl (**15**) and xanthone (**16**) in 51% and 4% yields, respectively. The NMR spectral data of the products are consistent with those previously reported for bixanthenyl and xanthone.[33,34] ^{1}H NMR (600 MHz, 25 °C, CD_2Cl_2): for **15**, δ 4.26 (s, 2H, C*H*), 6.71 (dd, *J* = 7.4, 1.6 Hz, 4H, Ar), 6.83 (d, *J* = 8.1 Hz, 4H, Ar), 6.95 (t, *J* = 7.4 Hz, 4H, Ar), 7.20−7.23 (m, 4H, Ar overlapping with Ar from xanthene starting material); for **16**, δ 7.40 (t, *J* = 7.5 Hz, 2H, Ar), 7.53 (d, *J* = 8.5 Hz, 2H, Ar), 7.76 (m, 2H, Ar), 8.30 (dd, *J* = 7.9, 1.7 Hz, 2H, Ar).

Oxidation of Cyclobutanol by $FeCl_3(\eta^1$-TEMPO) (385 mM Concentration). $FeCl_3(\eta^1$-TEMPO) (85.9 mg, 269.7 μmol) was dissolved in C_6D_6 (700 μL) to provide a purple solution. This corresponded to a $FeCl_3(\eta^1$-TEMPO) concentration of 385 mM. Addition of cyclobutanol (10 μL, 127.7 μmol) via microsyringe resulted in the immediate lightening of the solution, concomitant with the deposition of a maroon precipitate. The reaction mixture was allowed to stand without stirring for 10 min, whereupon it was filtered into an NMR tube through a basic alumina column (1 cm × 0.5 cm) supported on glass wool. The column was rinsed with C_6D_6 (0.5 mL), mesitylene (5 μL, 35.9 μmol) was added to the NMR tube via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed the complete consumption of cyclobutanol and formation of cyclobutanone in 75% yield. The NMR spectral data of the product were consistent with that previously reported for cyclobutanone.[68] ^{1}H NMR (600 MHz, 25 °C, C_6D_6): δ 1.20 (quintet, *J* = 8.2 Hz, 2H, C*H*$_2$), 2.47 (t, *J* = 8.2 Hz, 4H, C*H*$_2$).

Oxidation of Cyclobutanol by $AlCl_3(\eta^1$-TEMPO) (200 mM Concentration). $AlCl_3(\eta^1$-TEMPO) (40.6 mg, 140.2 μmol) was dissolved in CD_2Cl_2 (700 μL) and transferred to an NMR tube to provide a yellow solution. This corresponded to a $AlCl_3(\eta^1$-TEMPO) concentration of 200 mM. Addition of cyclobutanol (5 μL, 63.9 μmol) via microsyringe resulted in an immediate color change to orange, which then lightened to a very pale yellow within 30 min. Mesitylene (5 μL, 35.9 μmol) was added via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed complete consumption of cyclobutanol and formation of cyclobutanone in 100% yield. The NMR spectral data of the product were consistent with that previously reported for cyclobutanone.[68] ^{1}H NMR (500 MHz, 25 °C, CD_2Cl_2): cyclobutanone, δ 1.98 (quintet, *J* = 8.2 Hz, 2H, C*H*$_2$ overlapping with $AlCl_3(\eta^1$-TEMPOH)), 3.05 (t, *J* = 8.2 Hz, 4H, C*H*$_2$); $AlCl_3(\eta^1$-TEMPOH), δ 1.42 (s, 6H, C*H*$_3$), 1.54 (s, 6H, C*H*$_3$), 1.63−1.86 (m, 4H, C*H*$_2$), 1.95−2.02 (m, 2H, C*H*$_2$ overlapping with cyclobutanone), 7.14 (br s, 1H, N-*H*).

Oxidation of Cyclopropylcarbinol by $FeCl_3(\eta^1$-TEMPO) (260 mM Concentration). $FeCl_3(\eta^1$-TEMPO) (41.6 mg, 130.6 μmol) was dissolved in C_6D_6 (500 μL) to provide a purple solution. This corresponded to a $FeCl_3(\eta^1$-TEMPO) concentration of 260 mM. Addition of cyclopropylcarbinol (5 μL, 61.7 μmol) via microsyringe resulted in the immediate lightening of the solution, concomitant with the deposition of a maroon precipitate. The reaction mixture was allowed to stand without stirring for 30 min, whereupon it was filtered into an NMR tube through a basic alumina column (1 cm × 0.5 cm) supported on glass wool. The column was rinsed with C_6D_6 (0.5 mL), mesitylene (5 μL, 35.9 μmol) was added to the NMR tube via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed the complete consumption of cyclopropylcarbinol and formation of cyclopropanecarboxaldehyde in 84% yield. The NMR spectral data of the product were consistent with that previously reported for cyclopropanecarboxaldehyde (Supporting Information Figure S27).[69] ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ 0.28 (m, 2H, C*H*$_2$), 0.47 (m, 2H, C*H*$_2$), 1.27 (m, 1H, C*H*), 8.53 (d, *J* = 5.5 Hz, 1H, C*H*O).

Oxidation of Cyclopropylcarbinol by $FeCl_3(\eta^1$-TEMPO) (6.3 mM Concentration). $FeCl_3(\eta^1$-TEMPO) (1.0 mg, 3.14 μmol) was dissolved in C_6D_6 (500 μL) to provide a purple solution. This corresponded to a $FeCl_3(\eta^1$-TEMPO) concentration of 6.3 mM. Addition of cyclopropylcarbinol (1 μL of a 1.23 M stock solution, 1.23 μmol) via microsyringe resulted in the immediate lightening of the solution. The reaction mixture was allowed to stand without stirring for 30 min, whereupon it was filtered into an NMR tube through a basic alumina column (1 cm × 0.5 cm) supported on glass wool. The column was rinsed with C_6D_6 (0.5 mL), mesitylene (1 μL of a 0.72 M stock solution, 0.72 μmol) was added to the NMR tube via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed the complete consumption of cyclopropylcarbinol and formation of cyclopropanecarboxaldehyde in 98% yield. The NMR spectral data of the product were consistent with that previously reported for cyclopropanecarboxaldehyde.[69] No evidence for the formation of any ring-opened product was observed in the ^{1}H NMR spectrum of the reaction mixture. ^{1}H NMR (400 MHz, 25 °C, C_6D_6) δ 0.26 (m, 2H, C*H*$_2$), 0.45 (m, 2H, C*H*$_2$), 1.25 (m, 1H, C*H*), 8.52 (d, *J* = 5.5 Hz, 1H, C*H*O).

Oxidation of Cyclopropylcarbinol by $AlCl_3(\eta^1$-TEMPO) (190 mM Concentration). $AlCl_3(\eta^1$-TEMPO) (38.7 mg, 133.6 μmol) was dissolved in CD_2Cl_2 (700 μL) and transferred to an NMR tube to provide a yellow solution. This corresponded to a $AlCl_3(\eta^1$-TEMPO) concentration of 190 mM. Addition of cyclopropylcarbinol (5 μL, 61.7 μmol) via microsyringe resulted in an immediate color change to orange, which slowly lightened to a pale yellow over the course of 45 min. Mesitylene (5 μL, 35.9 μmol) was added via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed complete consumption of cyclopropylcarbinol and formation of cyclopropanecarboxaldehyde in 91% yield. The NMR spectral data of the product were consistent with that previously reported for cyclopropanecarboxaldehyde (Supporting Information Figure S28).[69] ^{1}H NMR (400 MHz, 25 °C, CD_2Cl_2): cyclopropanecarboxaldehyde, δ 1.04−1.11 (m, 4H, C*H*$_2$), 8.84 (d, *J* = 6.0

Hz, 1H, C*H*O), unassigned C*H* resonance overlaps with CH_2 resonance from $AlCl_3(\eta^1$-TEMPOH); $AlCl_3(\eta^1$-TEMPOH), δ 1.42 (s, 6H, CH_3), 1.54 (s, 6H, CH_3), 1.61−1.87 (m, 4H, CH_2 overlapping with cyclopropanecarboxaldehyde), 1.94−2.04 (m, 2H, CH_2), 7.15 (br s, 1H, N*H*).

Oxidation of Cyclopropylcarbinol by $AlCl_3(\eta^1$-TEMPO) (4.4 mM Concentration). $AlCl_3(\eta^1$-TEMPO) (0.9 mg, 3.11 μmol) was dissolved in CD_2Cl_2 (700 μL) and transferred to an NMR tube to provide a pale yellow solution. This corresponded to a $AlCl_3(\eta^1$-TEMPO) concentration of 4.4 mM. Addition of cyclopropylcarbinol (1 μL of a 1.23 M stock solution, 1.23 μmol) via microsyringe resulted in a color change to colorless over the course of 45 min. Mesitylene (1 μL of a 0.72 M stock solution, 0.72 μmol) was then added via microsyringe, and a ^{1}H NMR spectrum was recorded. Analysis of the chemical shifts and comparison of the product peak integrations with those of the internal standard revealed complete consumption of cyclopropylcarbinol and formation of cyclopropanecarboxaldehyde in 95% yield. The NMR spectral data of the product were consistent with that previously reported for cyclopropanecarboxaldehyde.[69] No evidence for the formation of any ring-opened product was observed in the ^{1}H NMR spectrum of the reaction mixture. ^{1}H NMR (400 MHz, 25 °C, CD_2Cl_2): cyclopropanecarboxaldehyde, δ 1.05−1.12 (m, 4H, CH_2), 8.85 (d, *J* = 6.0 Hz, 1H, C*H*O), unassigned C*H* resonance overlaps with CH_2 resonance from $AlCl_3(\eta^1$-TEMPOH); $AlCl_3(\eta^1$-TEMPOH), δ 1.43 (s, 6H, CH_3), 1.55 (s, 6H, CH_3), 1.62−1.88 (m, 4H, CH_2 overlapping with cyclopropanecarboxaldehyde), 1.95−2.05 (m, 2H, CH_2), 7.14 (br s, 1H, N*H*).

Reaction of $FeBr_3$ with TEMPO in Et_2O. An Et_2O solution (1 mL) of TEMPO (105.2 mg, 0.673 mmol) was added to a solution of $FeBr_3$ (204.1 mg, 0.691 mmol) in Et_2O (1 mL). An orange precipitate immediately formed. The reaction mixture was allowed to stand at room temperature for 5 h, whereupon the supernatant was filtered through a basic alumina column (1 cm × 0.5 cm) supported on glass wool to remove the metal containing products. The column was rinsed with Et_2O (1 mL). Analysis of the filtrate by GC/MS revealed the presence of 1,1-diethoxyethane and TEMPO (Supporting Information Figure S41). The retention times of 1,1-diethoxyethane and TEMPO were consistent with that of authentic material, recorded using the same conditions. The orange precipitate was then dissolved in CH_2Cl_2 (3 mL), and the resulting orange solution was filtered through a Celite plug supported on glass wool (1 cm × 0.5 cm). The dark orange filtrate was then layered with hexanes (5 mL), and subsequent storage at −25 °C for 12 h resulted in the deposition of an orange powder (236.0 mg). Analysis of this powder by ^{1}H NMR spectroscopy revealed the presence of complexes **23** and **24** in an approximate 3:2 ratio. ^{1}H NMR (400 MHz, 25 °C, CD_2Cl_2): for **23**, δ −1.14 (s, 2H, β-H), 8.18 (s, 1H, γ-H), 10.89 (s, 1H, γ-H), 12.47 (br s, 6H, CH_3), 16.02 (br s, 6H, CH_3), 59.20 (s, 2H, β-H), a resonance assignable to NH was not observed, likely due to paramagnetic broadening; for **24**, δ 1.72 (sh, 4H, CH_2), 2.02 (s, 12H, CH_3), 2.50 (s, 4H, CH_2), 3.73 (s, 12H, CH_3), 6.58 (s, 4H, CH_2), 47.18 (s, 2H, N*H*). GC/MS: *m/z* 1,1-diethoxyethane, 117 $[M - H]^+$, 103 $[C_5H_{11}O_2$ fragment$]^+$, 73 $[C_4H_9O$ fragment$]^+$, 45 $[C_2H_5O$ fragment$]^+$; TEMPO, 156 $[M]^+$.

Synthesis of $[FeBr_2(\eta^1$-TEMPOH)$]_2(\mu$-O) (24). An Et_2O solution (1 mL) of TEMPO (131 mg, 0.838 mmol) and 1,4-cyclohexadiene (80 μL, 0.846 mmol) was layered on to an Et_2O solution (2 mL) of $FeBr_3$ (229 mg, 0.774 mmol) that was previously filtered through a Celite plug supported on glass wool (1 cm × 0.5 cm). An orange precipitate immediately formed. The reaction mixture was allowed to stand at room temperature for 18 h, whereupon the resulting orange precipitate was isolated by decanting off the supernatant. This solid was recrystallized twice from CH_2Cl_2 solutions layered with Et_2O, which were stored at −25 °C for 12 h: 68.7 mg, 32% yield. ^{1}H NMR (400 MHz, 25 °C, CD_2Cl_2) δ 1.64 (sh, 4H, CH_2), 1.86 (s, 12H, CH_3), 2.36 (s, 4H, CH_2), 3.72 (br s, 12H, CH_3), 6.39 (s, 4H, CH_2), 47.21 (br s, 2H, N*H*). Anal. Calcd for $C_{18}H_{38}Br_4Fe_2N_2O_3$: C, 28.38, H, 5.03, N, 3.68. Found: C, 28.36, H, 5.29, N, 3.60. IR (KBr pellet, cm^{-1}): 3077 (s), 3021 (m), 2989 (m), 2970 (s), 2950 (s), 2876 (m), 1461 (m), 1397 (s), 1384 (s), 1367 (m), 1357 (m), 1336 (w), 1299 (w), 1246 (w), 1226 (m), 1204 (m), 1170 (m), 1117 (m), 1086 (w), 1062 (w), 1054 (w), 1026 (s), 988 (w), 974 (m), 945 (m), 870 (s), 744 (m), 712 (w), 635 (s), 565 (w), 499 (m), 427 (m), 412 (w).

Reaction of $FeBr_3$ with TEMPOH in Et_2O. An Et_2O solution (1 mL) of TEMPOH (57.8 mg, 0.368 mmol) was added to a solution of $FeBr_3$ (102.0 mg, 0.345 mmol) in Et_2O (3 mL). An orange precipitate immediately formed. Storage of this mixture at −25 °C for 12 h resulted in the deposition of more orange powder. The solid was then collected by decanting off the supernatant (101.5 mg). Analysis of this material by ^{1}H NMR spectroscopy revealed the presence of complexes **23** and **24**, in an approximate 1:1 ratio. ^{1}H NMR (400 MHz, 25 °C, CD_2Cl_2): for **23**, δ −1.37 (s, 2H, β-H), 7.89 (s, 1H, γ-H), 10.69 (s, 1H, γ-H), 12.31 (br s, 6H, CH_3), 15.75 (br s, 6H, CH_3), 58.60 (s, 2H, β-H), a resonance assignable to NH was not observed, likely due to paramagnetic broadening; for **24**, δ 1.70 (sh, 4H, CH_2), 1.93 (s, 12H, CH_3), 2.46 (s, 4H, CH_2), 3.69 (s, 12H, CH_3), 6.48 (s, 4H, CH_2), 47.09 (s, 2H, N*H*).

X-ray Crystallography. Data for **23** and **24** were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a Mo Kα X-ray source (α = 0.710 73 Å). Crystals were mounted on a cryoloop under Paratone-N oil, and all data were collected at 100(2) K using an Oxford nitrogen gas cryostream system. X-ray data for both **23** and **24** were collected utilizing frame exposures of 10 (low angle) and 15 s (high angle). Data collection and cell parameter determination were conducted using the SMART program.[70] Integration of the data frames and final cell parameter refinement were performed using SAINT software.[71] Absorption correction of the data was carried out using the multiscan method SADABS.[72] Subsequent calculations were carried out using SHELXTL.[73] Structure determination was done using direct methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom of attachment with the exception of the NH hydrogen atom. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[73] Further crystallographic details can be found in Supporting Information Table S1.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic details (as a CIF file), spectral data, and additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(25) Interestingly, oxidations with complex **1** appear to result in lower observed yields overall. However, this is likely an artifact of the reaction workup procedure. In particular, the products formed in the reaction with **1** are only observable by ^{1}H NMR spectroscopy after filtration through a basic alumina column, which is required to remove the paramagnetic byproduct, $FeCl_3(\eta^1\text{-TEMPOH})$ (see Experimental Section for more details). This filtration procedure likely results in some product loss on the alumina column. While this procedure is obviously not ideal, it was the only protocol we discovered that was able to separate the organic products from the paramagnetic iron-containing byproducts. In comparison, in most instances the analogous oxidations with **2** do not require removal of metal containing products via filtration through a basic alumina column for analysis by ^{1}H NMR spectroscopy. As a result, reactions with **2** often feature higher yields.
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