JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
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Tuning the Reactivity of TEMPO by Coordination to a Lewis Acid: Isolation and Reactivity of $MCl_3(\eta^1\text{-TEMPO})$ (M = Fe, Al)

Jeremiah J. Scepaniak, Ashley M. Wright, Richard A. Lewis, Guang Wu, and Trevor W. Hayton*

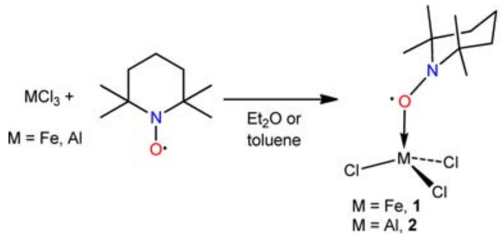
Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, United States

Supporting Information

ABSTRACT: Addition of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) to MCl_3 (M = Fe, Al) results in the formation of $MCl_3(\eta^1\text{-TEMPO})$ [M = Fe (**1**), Al (**2**)]. Both **1** and **2** oxidize alcohols to generate ketones or aldehydes along with the reduced complexes $MCl_3(\eta^1\text{-TEMPOH})$ [M = Fe (**3**), Al (**4**)]. Complexes **1**−**4** were fully characterized, including analysis by X-ray crystallography. Additionally, control experiments indicated that neither MCl_3 (M = Al, Fe) nor TEMPO are capable of effecting the oxidation of alcohols independently.

The catalytic aerobic oxidation of primary alcohols using the Cu/TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidine-*N*-oxyl) catalyst system has been the focus of considerable interest in recent years.[1−4] This protocol exhibits excellent functional group tolerance and displays high chemoselectivity. Similar procedures have been developed that utilize other metals, including Ru,[5] Mo,[6] Mn,[7] and Fe,[8] thereby expanding the substrate scope, especially toward 2° alcohols.[8,9] Importantly however, there is still considerable debate concerning the mechanisms of these transformations, despite significant effort dedicated to understanding this family of catalysts. For example, in the Cu/TEMPO system, several research groups favor a mechanism that involves hydride transfer to nitrogen,[10,11] while others favor a mechanism that involves H-atom transfer to oxygen.[12−15] Moreover, there is debate over whether coordination of the alcohol to the metal occurs during catalysis.[12,16] Theoretical studies have also failed to find consensus.[2,17,18] This uncertainty is perhaps surprising, considering the advantages of this protocol and also the widespread interest in proton-coupled electron transfer (PCET).[19,20] In this regard, a better mechanistic understanding of TEMPO coordination chemistry and reactivity could allow for improved substrate scope and the development of new transformations.

Our laboratory's interest in iron coordination chemistry[21] brought to our attention the aforementioned Fe/TEMPO oxidation protocol.[8] The proposed catalytic cycle involves hydride transfer from an alcohol to an Fe(III)−TEMPO adduct, generating Fe(II)−(TEMPOH) and an aldehyde. Similarly, MacMillan and co-workers proposed that an Fe(III)−TEMPO adduct mediates α-oxyamination of aldehydes.[22] However, there are no well-defined Fe(III)−TEMPO complexes in the literature to help evaluate these hypotheses. In fact, only one structurally characterized Fe−TEMPO complex is known, namely, the Fe(II) species $[PhB(MesIm)_3]Fe(TEMPO)$.[23] In light of the limited information concerning Fe−TEMPO coordination chemistry[22−25] and the uncertainty surrounding the mechanisms of TEMPO-mediated oxidations more generally, we endeavored to explore the reactivity of TEMPO with Fe(III). Herein we report the synthesis and characterization of the complexes $MCl_3(\eta^1\text{-TEMPO})$ (M = Fe, Al) and describe their oxidation of alcohols. These experiments provide insight into the mechanism of TEMPO-mediated oxidations and reveal the ability of Lewis acid coordination to modulate the reactivity of oxyl radicals.



(1)

We began by exploring the possibility of adduct formation between $FeCl_3$, a common Fe(III) synthon, and TEMPO in weakly coordinating solvents. Thus, layering an ethereal solution of TEMPO onto an ethereal solution of $FeCl_3$ followed by storage at −25 °C resulted in the deposition of purple crystalline blocks of $FeCl_3(\eta^1\text{-TEMPO})$ (**1**) in 73% yield (eq 1). ^1H NMR spectroscopy of these crystals in C_6D_6 revealed three broad resonances at 45.69, 6.45, and −29.62 ppm, integrating for 4, 12, and 2 H atoms, respectively. These resonances are assignable to the β, methyl, and γ protons of the TEMPO moiety. Complex **1** crystallizes in the orthorhombic space group *Pnma*. In the solid state, **1** exhibits a pseudotetrahedral coordination environment about the Fe center, comprising three chloride ligands and an η^1-TEMPO ligand (Figure 1). The Fe1−O1 and N1−O1 bond lengths are 1.8996(12) and 1.2975(17) Å, respectively (Table 1). For comparison, the N−O bond length in free TEMPO is 1.296(3) Å, while that in $SiCl_3(\eta^1\text{-TEMPO})$, which contains the anionic $[TEMPO]^-$ ligand, is 1.485(2) Å.[26] Additionally, the average Fe−Cl bond length is 2.180 Å, identical to that in $[FeCl_4]^-$ (av Fe−Cl = 2.18 Å, 232 examples).[27] These data suggest that the TEMPO ligand in **1** should be considered neutral, while the Fe center is best described as Fe(III). For further comparison, the M−O and N−O bond lengths in $[CuCl_2(\eta^1\text{-TEMPO})]_2$ are 1.940(1) and 1.276(2) Å, respectively,[16] while the M−O and

Received: September 25, 2012
Published: November 7, 2012

dx.doi.org/10.1021/ja309499h | *J. Am. Chem. Soc.* 2012, 134, 19350−19353

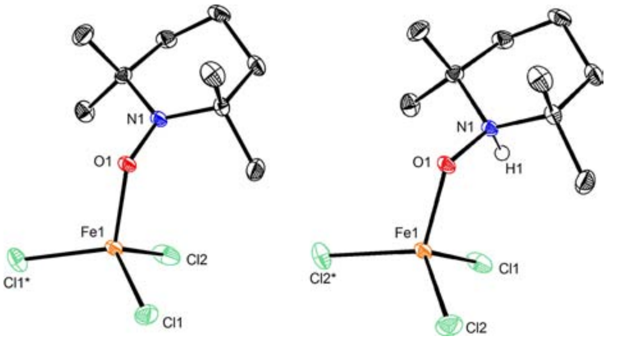


Figure 1. Solid-state molecular structures of (left) **1** and (right) **3**. Selected H atoms have been omitted for clarity.

Table 1. Comparison of Metrical Parameters of Complexes 1–4, TEMPO, and $SiCl_3(\eta^1$-TEMPO)

	M–O (Å)	N–O (Å)	av. M–Cl (Å)	∑(E–N–E)
1	1.8996(12)	1.2975(17)	2.180	356.9
2	1.8073(7)	1.3129(9)	2.121	356.2
3	1.8840(8)	1.4006(11)	2.189	339.2
4	1.7745(8)	1.4014(10)	2.129	338.7
TEMPO[a]	–	1.296(3)	–	356.3
$SiCl_3(\eta^1$-TEMPO)[a]	1.619(1)	1.485(2)	2.024	331.3

[a] Data taken from ref 26.

N–O bond lengths in $Cu(hfac)_2(\eta^1$-TEMPO) (hfac = $[OC(CF_3)CH(CF_3)CO]^-$) are 1.920(5) and 1.269(7) Å, respectively.[28] These parameters are similar to those exhibited by **1**, and like **1**, both Cu complexes feature a neutral TEMPO ligand.

Complex **1** exhibits an effective magnetic moment of $4.72\mu_B$ at 300 K, as determined by SQUID magnetometry (Figure 2). This value is consistent with an $S = 2$ ground state and can be explained by invoking strong antiferromagnetic coupling between the TEMPO ligand and the $S = {}^5/_2$ spin state of the high-spin Fe(III) center. Similar strong antiferromagnetic coupling in TEMPO complexes has been observed previously.[16,28–31] The magnetic data were modeled in julX using $S = 2$, $g_1 = 1.95$, and $D_1 = 7.0$ cm^{-1}.[32] Interestingly, this model exhibited somewhat poor agreement with the experimental data below 30 K, likely because of intermolecular antiferromagnetic interactions [see the Supporting Information (SI)].

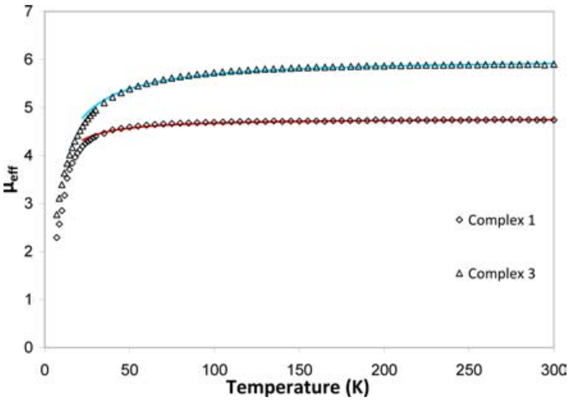


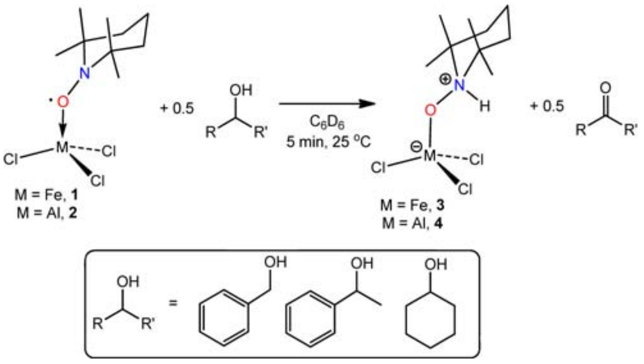
Figure 2. Solid-state magnetic susceptibility data for **1** and **3** from 4 to 300 K.

To obtain further support for the proposed electronic structure of **1**, we endeavored to synthesize an analogue that incorporated a redox-inactive metal. Thus, addition of TEMPO to a toluene slurry of $AlCl_3$ resulted in the rapid formation of an amber solution. Upon workup, yellow crystalline blocks of $AlCl_3(\eta^1$-TEMPO) (**2**)[33] were isolated in 72% yield (eq 1). The ^1H NMR spectrum of **2** in C_6D_6 consists of three broad resonances at 20.61, −2.96, and −29.49 ppm, integrating for 2, 12, and 4 H atoms, respectively. These are assignable to the γ, methyl, and β protons of the TEMPO ligand. Also present in the NMR spectrum are signals due to a small amount of a diamagnetic product, identifiable as $AlCl_3(\eta^1$-TEMPOH) (**4**) (see below). Complex **2** exhibits an effective magnetic moment of $1.68(2)\mu_B$ at 300 K in C_6D_6, as determined by Evans' method.[34] This value is consistent with an $S = {}^1/_2$ ground state and is similar to that expected for an oxyl radical.[35,36] Interestingly, complex **2** has been previously generated in situ and studied by EPR spectroscopy.[33,37]

Complex **2** is isomorphous with its Fe analogue in the solid state. It exhibits Al1–O1 and N1–O1 bond lengths of 1.8073(7) and 1.3129(9) Å, respectively (Table 1). The shorter M–O bond in **2** in comparison with that in **1** is consistent with the smaller ionic radius of Al^{3+},[38] while the similarity of its N–O bond length with that in **1** further confirms the M(III)–(TEMPO·) electronic structures proposed for these complexes.

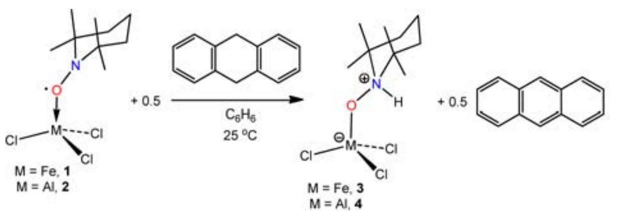
With complexes **1** and **2** in hand, we endeavored to explore their reactivity with alcohols. Addition of 0.5 equiv of benzyl alcohol to a deep-purple solution of **1** in C_6D_6 instantaneously produced a bright-yellow solution. ^1H NMR spectroscopy of this mixture revealed the consumption of **1** and formation of a new paramagnetic product, $FeCl_3(\eta^1$-TEMPOH) (**3**) (Scheme 1), as revealed by diagnostic resonances at 50.86 and 15.26 ppm (Figure S8 in the SI). Filtration of this solution through basic alumina removed the paramagnetic product, allowing for the observation of benzaldehyde, as indicated by a sharp resonance at 9.66 ppm. Similarly, addition of 0.5 equiv of 1-phenylethanol or cyclohexanol to a C_6D_6 solution of **1** resulted in the formation of acetophenone or cyclohexanone, respectively (see the SI). Complex **1** could also oxidize 1-octanol, as evidenced by the formation of **3** (Figure S11); however, this reaction generated a complex mixture of organic products. The oxidation of 9,10-dihydroanthracene (DHA) was also possible, resulting in the clean formation of anthracene, but the reaction was substantially slower than those with alcohols.

Scheme 1



Fortuitously, X-ray-quality crystals of the iron-containing product **3** precipitated from the DHA reaction mixture upon standing for 24 h at room temperature. An X-ray diffraction study revealed that complex **3** is isomorphous with complexes **1** and **2**, exhibiting a pseudotetrahedral coordination environment about the Fe center; however, the metrical parameters of the TEMPO ligand indicate a change in TEMPO oxidation state. In particular, the N1−O1 bond length in **3** is 1.4006(11) Å and the sum of the angles around N1 is 339.2° (Table 1), consistent with the presence of $[\mathrm{TEMPO}]^-$.[26] Additionally, a hydrogen atom was located in the difference map and successfully refined on N2. This binding mode of TEMPOH has been observed in only a few instances.[24,39,40] Finally, the average Fe−Cl (2.189 Å) and Fe−O [1.8840(8) Å] bond lengths are comparable to those in **1**, suggesting the presence of an Fe^{3+} center in **3**.

Complex **3** was isolated in 81% yield as a pale-pink crystalline solid by the addition of 0.5 equiv of DHA to **1** in C_6H_6 (eq 2).



(2

Complex **3** could also be isolated in 53% yield by addition of benzyl alcohol to **1** in C_6H_6. The ^{1}H NMR spectrum of **3** in C_6D_6 exhibits two broad resonances at 14.97 and 5.75 ppm, assignable to two unique methyl environments. The inequivalence of the methyl groups is consistent with the TEMPOH binding mode found in the solid state. A resonance assignable to the NH proton could not be definitively identified by NMR spectroscopy; however, a sharp NH stretch was observed at 3079 cm^{-1} in its IR spectrum. Finally, complex **3** exhibits an effective magnetic moment of $5.74\mu_B$ at 300 K, as determined by SQUID magnetometry (Figure 2). This value is consistent with the $S = {}^5/_2$ ground state expected for a high-spin Fe(III) center[41] and can be modeled using $S = {}^5/_2$, $g_1 = 2.037$, and $D_1 = 12.0\ \mathrm{cm}^{-1}$.[32]

Interestingly, addition of 0.5 equiv of benzyl alcohol, cyclohexanol, or 1-phenylethanol to a C_6D_6 solution containing **2** resulted in immediate oxidation of the alcohol and formation of a new Al-containing product, $AlCl_3(\eta^1\text{-TEMPOH})$ (**4**) (Scheme 1). 1-Octanol was also oxidized under these conditions, but as in the iron reaction, a complex mixture of products was generated (Figure S18). Conveniently, in the reaction of DHA with **2**, X-ray-quality crystals of **4** precipitated from the reaction mixture. Complex **4** is isostructural with complex **3** and exhibits similar metrical parameters for the TEMPOH ligand. For example, the N1−O1 bond length in **4** is 1.4014(10) Å and the sum of the angles around N1 is 338.7° (Table 1).[26] As observed for **3**, a hydrogen atom was located and successfully refined on N1, while the Al−Cl (av 2.129 Å) and Al−O [1.7745(8) Å] bond lengths are comparable to those in **2**.

On a preparative scale, addition of 1 equiv of DHA to **2** in C_6H_6 resulted in the rapid formation of a colorless solution and deposition of colorless crystalline blocks of **4** in 79% yield (eq 2). Complex **4** could also be isolated in 61% yield by addition of benzyl alcohol to **2** in C_6H_6. The ^{1}H NMR spectrum of **4** in C_6D_6 revealed two resonances at 1.20 and 0.70 ppm assignable to two different methyl environments, while a singlet at 6.90 ppm is assignable to the NH proton.[39] Overall, these data confirm the TEMPOH binding mode found in the solid state.

The isolation and characterization of **3** and **4** unambiguously reveals the destination of the H atom upon abstraction by **1** and **2**, respectively. In addition, the observation that complex **2**, which contains redox-inactive Al, is a competent oxidant demonstrates that a redox change at the metal is not necessary for substrate oxidation. This latter point is perhaps the most important, as almost every mechanistic scheme invokes redox cycling of the metal center.[8,12,13,16] Our experiments allow us to make other mechanistic inferences as well. In particular, the oxidation of DHA by **1** and **2** (eq 2) demonstrates that coordination of the substrate to the metal center is not required for H-atom transfer, as DHA is unlikely to coordinate to the metal. However, the stark difference in the reaction times for DHA and alcohols suggests that two different mechanisms may be operative and that in the case of alcohols, a metal−alcohol adduct may be formed during the transformation. Finally, control experiments indicated that neither MCl_3 (M = Al, Fe) nor TEMPO are capable of effecting the oxidation of benzyl alcohol independently (see the SI), demonstrating the synergistic role of MCl_3 and TEMPO in the transformation.

The observed selectivity of **1** and **2** is also consistent with previous systems. Liang and co-workers reported that the Fe/TEMPO protocol is competent for oxidation of both 1° and 2° alcohols,[8,9] while most Cu/TEMPO protocols are unable to efficiently oxidize 2° alcohols such as cyclohexanol.[1,16,42,43] The difference in selectivity may be related to the binding mode of TEMPO in these two systems. Previously, Rey and co-workers reported that $CuBr_2(\eta^2\text{-TEMPO})$,[16] in which the TEMPO ligand is bound through both nitrogen and oxygen, could oxidize 1-octanol but not 3-octanol at room temperature, suggesting a steric component to the selectivity.

We suggest that the transformation proceeds via a mechanism involving concerted proton-coupled electron transfer (CPET) from the C−H bond of the substrate to the nitrogen atom of **1** or **2**.[19,20] generating complex **3** or **4**, respectively, and a ketyl radical. The latter is then quickly oxidized by a second equivalent of **1** or **2** to form the aldehyde or ketone. Alternately, H-atom transfer could occur at the oxygen of TEMPO, with subsequent isomerization to the N-bound form observed in **3** and **4**. Interestingly, Hoffman and co-workers showed that the spin density on the nitrogen atom of TEMPO increases upon Lewis acid coordination, suggesting greater radical character at that site,[33,37,44] an observation which would appear to support the initial transfer to nitrogen.

On the basis of bond strength considerations, TEMPO [TEMPOH bond dissociation free energy (BDFE) = 65.2 kcal mol^{-1}, C_6H_6][19] should not be able to effect the oxidation of DHA (BDFE = 76.0 kcal mol^{-1}, DMSO)[19,45] or cyclohexanol (bond dissociation energy = 92.4 kcal mol^{-1}).[46] Thus, it appears that the coordination of TEMPO to a Lewis acid increases the BDFE of TEMPOH by making TEMPO either a better oxidant or a better base.[19] We prefer the former rationale, as coordination of an alcohol (in this case $[\mathrm{TEMPOH}]^{\bullet+}$) to a metal generally decreases its $\mathrm{p}K_a$.[47] It is also possible that by employing even stronger Lewis acids we may be able to activate a broader range of C−H bonds. Erker and co-workers recently reported that frustrated Lewis pair-derived oxyl radicals are potent H-atom abstractors,[48,49] demonstrating that the reactivity of oxyl radicals can be greatly modified by changing the substituents attached to the nitrogen.

Our work shows that coordination to a metal ion is another way to modify the reactivity of an oxyl radical.

In conclusion, addition of TEMPO to MCl_3 (M = Fe, Al) results in the formation of the isolable adducts $MCl_3(\eta^1$-TEMPO) (M = Fe, Al). Upon coordination to the Lewis acid, TEMPO is activated toward the oxidation of both alcohols and 9,10-dihydroanthracene. Importantly, the latter reaction demonstrates that substrate coordination to the metal ion is not necessary for oxidation to occur, while the ability of $AlCl_3(\eta^1$-TEMPO) to oxidize alcohols indicates that metal-based redox changes are not necessary either. These findings may have mechanistic implications for other metal-catalyzed TEMPO oxidation protocols. In future work, we plan to interrogate further the mechanism of H-atom transfer in this system and will attempt to expand the substrate scope beyond alcohols.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, crystallographic details (CIF), spectral data for **1−4**, alcohol oxidations, and control reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

hayton@chem.ucsb.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Science Foundation (CHE 1059097) and the Alfred P. Sloan Foundation for financial support.

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