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Synthesis and Catalytic Reactivity of a Dicopper(II) μ-η^2:η^2-Peroxo Species Supported by 1,4,7-Tri-*tert*-butyl-1,4,7-triazacyclononane

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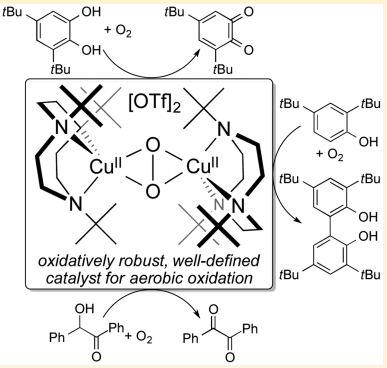
Supporting Information

ABSTRACT: O_2-derived Cu_nO_2 adducts are attractive targets for aerobic oxidation catalysis because of their remarkable reactivity, but oxidation of the supporting ligand limits catalytic turnover. We report that ^{t}Bu$_3$tacn (1,4,7-tri-*tert*-butyl-1,4,7-triazacyclononane) supports a dicopper(II) μ-η^2:η^2-peroxo species with the highest solution stability outside of an enzyme. Decomposition of this species proceeds without oxidation of the ^{t}Bu$_3$tacn ligand. Additive-free catalytic aerobic oxidation reactions at or above room temperature are described, highlighting the potential of oxidatively robust ligands in aerobic copper catalysis.



INTRODUCTION

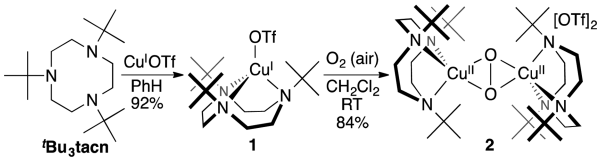
Cu^I-containing enzymes activate O_2 to generate Cu_nO_2 species capable of oxidizing substrates ranging in reactivity from catechol to methane.[1] Low-temperature oxygenation of synthetic Cu^I compounds has provided a wealth of structurally and spectroscopically characterized Cu_nO_2 species, which, together with their reactivity profiles, have informed on metalloenzyme structure and function.[2] However, applying these reactive Cu_nO_2 species to catalysis has been elusive, as irreversible ligand oxidation can limit reactivity studies to stoichiometric oxidation at cryogenic temperatures.[2b,3] The most stable Cu_nO_2 adduct to date has a remarkable solution $t_{1/2}$(25 °C) of 25.5 h,[4] compared to typical values of seconds or shorter;[5] however, no catalytic studies have been reported. Ligands that support Cu_nO_2 adducts that resist decomposition long enough in solution at room temperature for biomimetic catalysis have been described,[5,6] and improving the ligand stability may yield new well-defined catalytic aerobic oxidation methods.

R_3tacn ligands (1,4,7-R_3-1,4,7-triazacyclononane, where R = Bn or ^{i}Pr) have long been known to support dicopper(III) bis-μ-oxo (**O**) and dicopper(II) μ-η^2:η^2-peroxo (**P**) cores at −80 °C,[7] but these Cu_2O_2 species are susceptible to oxidation of the nitrogen substituent at the weak C−H bonds of the α-carbon.[3b,8] We recently reported the first synthesis of ^{t}Bu$_3$tacn,[9] which lacks these reactive C−H bonds. Herein, we detail the synthesis of a **P** complex supported by ^{t}Bu$_3$tacn that is the most stable Cu_nO_2 species in solution outside of an enzyme. This stability has allowed its application to room-temperature aerobic oxidation catalysis without detectable oxidation of ^{t}Bu$_3$tacn.

RESULTS AND DISCUSSION

Synthesis and Characterization. [(^{t}Bu$_3$tacn)-Cu^I(MeCN)][PF_6] (**A**)[9] is relatively inert to O_2 compared to other [(R_3tacn)Cu^I(MeCN)]$^+$ complexes,[7a,c−e] where solutions of **A** begin to take on a light green color after a few hours at room temperature in CH_2Cl_2. This poor O_2 reactivity suggests that the Cu^I ion in **A** is sterically inaccessible to associative substitution. The acetonitrile ligand in **A** could not be removed by heating under vacuum, so we targeted a (^{t}Bu$_3$tacn)Cu^I complex with a labile counterion. Combining ^{t}Bu$_3$tacn with 0.5 equiv of (Cu^IOTf)$_2$·(C_6H_6) in benzene produced light yellow [(^{t}Bu$_3$tacn)Cu^I(OTf)] (**1**, Scheme 1).[10] CH_2Cl_2 solutions of **1**

Scheme 1. Synthesis of 1 and 2



rapidly develop a persistent dark brown color when exposed to air at room temperature. Dark brown-black crystals of oxidation product **2** were grown overnight in 84% yield. ^{1}H nuclear magnetic resonance (NMR) spectroscopy revealed that **2** is a diamagnetic species, consistent with the antiferromagnetic coupling seen with other Cu_2O_2 complexes.[3c] Crystals of **2** revealed a **P** complex (Figure 1) that features a planar Cu_2O_2

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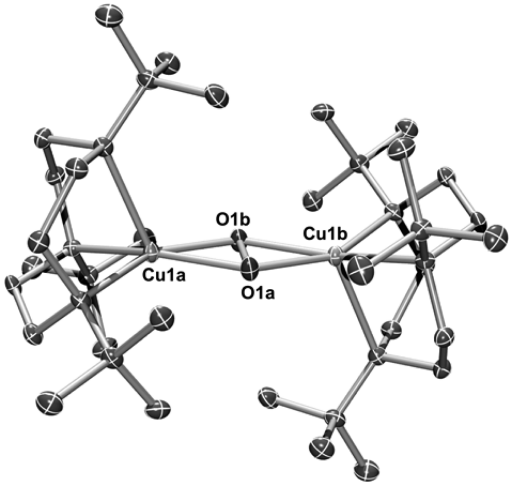

Figure 1. Molecular structure of the dication in **2**. Relevant distances: O1a−O1b, 1.475(4) Å; Cu1a···Cu1b, 3.6349(8) Å.

core with a Cu···Cu distance of 3.6349(8) Å and an O−O bond length of 1.475(4) Å. The high crystalline yield of **2** is consistent with an increased stability compared to related R_3tacn compounds. **2** features the longest Cu···Cu distance of any crystallographically well-resolved **P** species,[4,11] likely resulting from steric repulsion between the two ^{t}Bu$_3$tacn ligands. The O−O bond in **2** is of intermediate length, but given the error in O−O bond lengths reported for crystallographically characterized **P** species, we turned to resonance Raman spectroscopy as a more sensitive tool for determining O−O bond strength.

P complexes are often observed to equilibrate in solution with their redox-isomeric **O** form,[7a,12] a rearrangement involving an ∼0.7 Å Cu···Cu contraction.[3c] These isomers are differentiated in solution by their electronic spectra and $^{16}O_2/^{18}O_2$-dependent resonance Raman features.[2g,3b,c,13] **2** is soluble in MeCN and MeOH, as well as in H_2O containing Na_2HPO_4 or NaH_2PO_4 as a source of water-solubilizing anions. The electronic spectra of **2** in each solvent are nearly identical and are consistent only with the **P** form (Figure 2 and Figure S1). The resonance Raman spectrum of **2** in MeOH at room temperature reveals a resonance-enhanced mode at 773 cm^{-1}, which shifts to 729 cm^{-1} when **2** is formed from $^{18}O_2$ (Figure 2, inset). The resonance Raman spectrum is featureless in the region where modes associated with **O** species are found (580−650 cm^{-1}).[13] Therefore, the **O** form of **2**, if present at all, exists below the detection limits of resonance Raman and electronic absorption spectroscopies.[14] On the basis of the results of resonance Raman spectroscopy, **2** contains, to the best of our knowledge, the strongest O−O bond of all reported **P** species,[2a,3c] whereas the closely related **P** species $[(^iPr_3tacn)_2(Cu^{II})_2(O_2)][OTf]_2$ (**B**) features the weakest O−O bond (O−O stretch of 713 cm^{-1}).[12c] The stark difference between the O−O bonds in **B** and **2** is consistent with steric pressure between the two ^{t}Bu$_3$tacn ligands in **2** preventing approach of the copper ions to the extent possible in **B**, and we have shown that ^{i}Pr$_3$tacn is significantly smaller than ^{t}Bu$_3$tacn.[9] Despite this difference in O−O bond strength, both **2** and **B** maintain O_2 ligation when sparged with N_2 or subjected to vacuum, and no $^{16}O_2/^{18}O_2$ scrambling in **2** is observed in solution at room temperature. Furthermore, the charge-transfer transition of **2** at 398 nm is at an energy lower than those of typical **P** species (340−380 nm), suggesting unusually weak Cu−N and/or Cu−O bonding[3c,11c,15] enforced by the bulky ^{t}Bu$_3$tacn ligands. We postulate that the **O** form of **2** is not accessible because the requisite ∼0.7 Å Cu···Cu contraction is sterically prevented by the ^{t}Bu$_3$tacn ligands. This notion is corroborated by the remarkable stability of **2** toward ligand oxidation (see below). **O** forms are reactive to H-atom abstraction, and this isomer is typically implicated in ligand C−H oxygenation.[3b,16] Therefore, the stability of **2** toward intramolecular oxidation may reflect the inaccessibility of the **O** isomer, but the redox resistance of the ^{t}Bu groups may also contribute. The stability of **2** may also arise from the strength of the O−O bond, although Solomon and Karlin demonstrated that O−O bond strength in **P** complexes does not necessarily correlate with reactivity.[11c]

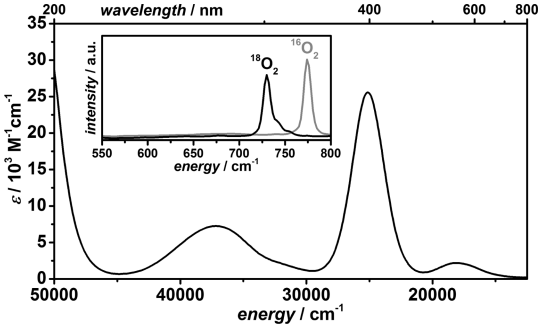

Figure 2. Electronic absorption spectrum of **2** in H_2O containing Na_2HPO_4. The inset shows the room-temperature resonance Raman spectrum (MeOH) of **2** derived from $^{16}O_2$ (gray) and $^{18}O_2$ (black) (excitation wavelength of 514.5 nm).

Solution Stability. We next examined the stability of **2** in solution. The absorption bands of **2** bleach exponentially in MeCN and MeOH, providing $t_{1/2}$(25 °C) values of 2.5 and 14.2 h, respectively. Anaerobic decomposition of **2** in MeOH afforded an intermediate that regenerated **1** in tetrahydrofuran (see the Supporting Information), supporting the idea that **2** could be employed in catalytic oxidations. Ligand extraction after decomposition reveals that ^{t}Bu$_3$tacn is not oxidized, and ^{1}H NMR and electronic absorption spectra reveal that **2** cleanly decomposes in MeCN to **A**. Formation of this species aligns with reports that coordinating solvents can displace O_2 from **P** species.[4b,17] **2** dissolved in aqueous Na_2HPO_4 shows unprecedented stability, with a $t_{1/2}$(25 °C) of 9.6 days. Interestingly, the half-life of **2** decreases to 6.7 days in aqueous NaH_2PO_4, suggesting a pH dependence on stability. In any case, **2** is the most solution-stable Cu_nO_2 coordination compound reported to date. With this remarkable stability to decomposition established, we began probing whether catalytic aerobic substrate oxidation could be achieved with **2**.

Reactivity. Inspired by tyrosinase enzymes,[1,2f,18] we explored the reactivity of **2** toward phenol, sodium phenolate, and phenol/NEt_3. **2** is inert to these substrates in D_2O or CD_3OD at 25 and 50 °C, in stark contrast to other **P** species[5,6,19] known to react with these substrates at cryogenic temperatures.[3a,b,20] The inability of O_2 to associatively displace MeCN from **A** may indicate that the ^{t}Bu groups in **2** impede the approach of the substrate to copper. Tyrosinase reactivity follows an associative mechanism,[20g] so the inaccessibility of copper in **2** likely explains its stability to these substrates. The aerobic oxygenation of substituted phenolic substrates has been advanced in recent years to catalytic systems,[5,6] with results from Lumb

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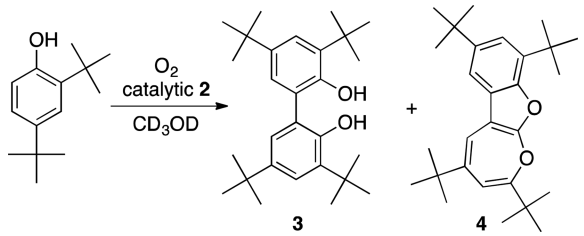
demonstrating a simple and scalable system,[21] and we therefore targeted oxidation of more electron-rich phenolic substrates. **2** is reactive to 2,4-di-*tert*-butylphenol in MeOH, favoring C−C bond formation to **3** over arene oxygenation (Table 1). **B**

Table 1. Catalytic Aerobic Oxidation of 2,4-Di-*tert*-butylphenol with 2[a]



catalyst loading (mol %)	temp	time (h)	yield of **3** (%)[b]	yield of **4** (%)[b]
19	room temperature	66	36	2
20	50 °C	3	52	15
21	65 °C	3	29	15

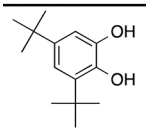
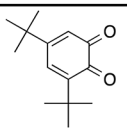
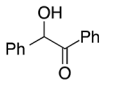
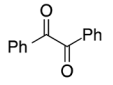
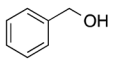
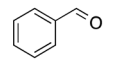
[a]Reactions run under an O_2 balloon. [b]^{1}H NMR spectroscopic yields based on an internal standard (1,3,5-trimethoxybenzene).

similarly provided **3** when exposed to 2,4-di-*tert*-butylphenol at −78 °C, although the reaction was not catalytic.[7e] The mechanism of oxidation is unclear but is unlikely to involve outer-sphere electron transfer based on ongoing electrochemical studies.[22] Phenolic C−C coupling is often attributed to the **O** isomer of Cu_2O_2 cores[3b] and may indicate that the **O** isomer (or another reactive isomer) is present in solutions of **2** below the detection limits of resonance Raman and electronic absorption spectroscopies. Unlike **B**, **2** is competent for catalytic oxidation of 2,4-di-*tert*-butylphenol (Table 1), where the direct C−C-coupled biphenol oxidation product **3** may be further oxidized to benzoxepine **4** as has been noted in previous systems,[23] with an increased level of benzoxepine formation at higher temperatures. It should be noted that ^{t}Bu$_3$tacn ligation is verified throughout each reaction by ^{1}H NMR spectroscopy, and that no free ligand is observed in any reaction we describe here, consistent with oxidative C−C coupling by a discrete (^{t}Bu$_3$tacn)Cu species.

Another common substrate class for Cu_2O_2 species is catechols. **2** is inert to catechol in water and MeOH but is competent for catalytic aerobic oxidation of 3,5-di-*tert*-butylcatechol to 3,5-di-*tert*-butyl-*o*-benzoquinone at room temperature (Table 2). **B** was shown to react stoichiometrically with 3,5-di-*tert*-butylcatechol at −80 °C to afford a (^{i}Pr$_3$tacn)-Cu^{II}-supported semiquinonato species, which may arise from trapping of the Cu^I ion by the newly formed quinone product.[24] With **2**, formation of a stable copper−semiquinonato adduct is sterically unfavorable, which, together with the oxidative stability of ^{t}Bu$_3$tacn compared to ^{i}Pr$_3$tacn, likely accounts for catalysis by **2**. Throughout catalysis, **2**, 3,5-di-*tert*-butylcatechol, and 3,5-di-*tert*-butyl-*o*-benzoquinone are the only species observed by ^{1}H NMR spectroscopy; free ^{t}Bu$_3$tacn or oxidized forms of this ligand are not observed.

Because **2** is competent for catalytic oxidation, we reasoned that substrates typically capable of reducing Cu^{II} ions would also be viable for catalysis. Copper(II) salts, particularly in conjunction with nitroxyl radicals, are efficient catalysts for alcohol oxidation.[25] Additionally, Stack demonstrated that

Table 2. Scope of Aerobic Oxidation by 2[e]

substrate	product	catalyst loading (mol%)	temp. (°C)	yield (time)[a]
		21	r.t.	91%[b] (24h)
		23	50	73%[b] (4h)
		19	65	70%[b] (2h)
		20	r.t.	92% (4h)
		20	50	100% (1h)
		5	50	93% (29h)[c]
		*stoich.*	r.t.	0%[d]
		stoich.	50	9% (76h)[d]
		stoich.	65	34% (76h)[d]

[a]Yield based on ^{1}H NMR spectroscopy with an internal standard (1,3,5-trimethoxybenzene or 1,3,5-tri-*tert*-butylbenzene). [b]Complete consumption of the starting material; no other products observed. [c]Reaction run open to the atmosphere. [d]Yield based on GC with an internal standard (1,3,5-tri-*tert*-butylbenzene); reaction run in CH_3OH. [e]Reactions run under an O_2 balloon in CD_3OD unless otherwise specified.

benzyl alcohol is stoichiometrically oxidized by **P** and/or **O** species at −40 °C.[26] These studies prompted us to investigate the catalytic competence of **2** for aerobic alcohol oxidation. Indeed, **2** is competent for the catalytic oxidation of benzoin to benzil at room temperature (Table 2). We next turned to less activated alcohols, finding that **2** is capable of very slow, substoichiometric oxidation of benzyl alcohol at 50 °C. As with other substrates, ^{t}Bu$_3$tacn was verified by ^{1}H NMR spectroscopy to remain bound and unoxidized throughout each reaction. While **2** is not an efficient aerobic alcohol oxidation catalyst, we are currently exploring whether smaller ligands with oxidative robustness similar to that of ^{t}Bu$_3$tacn could allow catalytic oxidation with improved substrate scope. Lumb has recently extended alcohol oxidation by **P** and/or **O** complexes to room-temperature catalytic alcohol oxidation in the absence of TEMPO,[27] and while **2** is not an efficient catalyst for such reactions, **2** provides a unique opportunity to explore the mechanism by which well-defined **P** species oxidize alcohols to carbonyl products.

CONCLUSIONS

In conclusion, we have shown that ^{t}Bu$_3$tacn supports the most stable **P** coordination complex reported to date. Because intramolecular oxidation was undetectable at room temperature, we were able to take advantage of intermolecular oxidation in the catalytic aerobic oxidation of three substrates at or near room temperature without additives and found that ^{t}Bu$_3$tacn is also robust under catalytic conditions. The robustness of ^{t}Bu$_3$tacn coordination throughout oxidation provides a unique opportunity to probe catalytic oxidation mechanisms within a well-defined system. While only the **P** isomer is spectroscopically detected in solutions of **2**, substrate reactivity implicates the intermediacy of the **O** isomer (or another reactive isomer), underscoring the oxidative robustness of ^{t}Bu$_3$tacn. Finally, we are working to expand the substrate scope by developing novel ligands with improved steric accessibility but robustness to oxidation similar to that of

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$^{t}Bu_3tacn$ to extend the usefulness of Cu_2O_2 systems in selective oxidation catalysis.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed in glovebox (UNI-LAB MBRAUN) or using a Schlenk technique unless otherwise specified. Solvents CH_2Cl_2 and Et_2O used in reactions were obtained from a solvent purification system (MB-SPS MBRAUN). All other glovebox solvents were obtained from commercial sources and dried over activated molecular sieves. Copper(I) trifluoromethanesulfonate benzene complex (technical grade, 90%, Sigma-Aldrich) required purification as follows. In a glovebox, the crude solid was heated in benzene for 30 min at 75−80 °C. The resulting solution was then filtered hot over Celite, and the solvent was removed in vacuo to yield a white air/solvent sensitive powder. Purification was performed immediately prior to usage for best results. All other chemicals and solvents were obtained from commercial sources and used as received.

Complex Syntheses. *[($^{t}Bu_3tacn$)Cu^{I}(MeCN)][PF_6] (**A**).* The following procedure is modified from the original report.[9] In a round-bottom flask equipped with a stir bar, tetrakis(acetonitrile)-copper(I) hexafluorophosphate (1.24 g, 3.33 mmol, 1 equiv) and $^{t}Bu_3tacn$ (1.02 g, 3.43 mmol, 1.03 equiv) were dissolved/suspended in acetonitrile. The reaction mixture was stirred for 30 min, at which time the solution appeared to be clear and colorless. The reaction mixture was filtered over Celite through a glass-sintered frit. The solvent was removed to yield 1.74 g (3.17 mmol, 95% yield) of pure copper complex as a white solid. The characteristics of the ^{1}H NMR and IR spectra matched spectroscopic values reported previously for this compound.

*($^{t}Bu_3tacn$)Cu^{I}(OTf) (**1**).* In a glovebox, copper(I) trifluoromethanesulfonate benzene complex (0.1218 g, 0.242 mmol, 1 equiv) and $^{t}Bu_3tacn$ (0.144 g, 0.484, 2 equiv) were added to a 20 mL glass vial with a stir bar. Benzene (10 mL) was added to the vial, which was then capped, and the solution was stirred for 1 h. The solvent was removed in vacuo to yield the product as an off-white powder (0.2288 g, 0.449 mmol, 92%). Note that **1** is very reactive to trace acetonitrile in the glovebox atmosphere, forming [($^{t}Bu_3tacn$)Cu^{I}(MeCN)][OTf]$_2$ (**A**), and was accordingly handled in only an acetonitrile-free glovebox: ^{1}H NMR (400 MHz, C_6D_6) δ 2.43−2.26 (6H, m), 1.59−1.41 (6H, m), 1.10 (27H, s); IR (KBr) 3019, 2976, 2911, 2844, 1638, 1497, 1480, 1449, 1402, 1368, 1265 (br, sh), 1226, 1195, 1165, 1150, 1097, 1033, 935, 892, 845, 804, 759, 726, 690, 638, 571, 518, 474 cm^{-1}.

*[($^{t}Bu_3tacn$$Cu^{I}$)$_2$($\mu$-$\eta^2$:$\eta^2$-$O_2$)][OTf]$_2$ (**2**).* A vial containing **1** (0.2288 g, 0.449 mmol) was removed from the glovebox. DCM (10 mL) was added to the vial exposed to air, causing the resulting solution to immediately flush dark brown. The vial was left open to the air overnight for slow evaporation. The resulting crystals were washed with chloroform to yield the product as dark brown crystals (0.1996 g, 0.423 mmol, 84%): ^{1}H NMR (400 MHz, CD_3OD) δ 3.31−3.20 (12H, m), 2.68−2.54 (12H, m), 1.85−1.10 (54H, br s); positive-mode NSI-MS m/z (relative intensity, formula, ppm) 360.24400 {39.40%, [($^{t}Bu_3tacn$)Cu]$^+$ ($C_{18}H_{39}{}^{63}CuN_3^+$), Δ = 1.5 ppm}, 362.24231 {18.09%, [($^{t}Bu_3tacn$)Cu]$^+$ ($C_{18}H_{39}{}^{65}CuN_3^+$), Δ = 1.8 ppm}, 752.47890 {97.51%, [($^{t}Bu_3tacn$)$_2$$Cu_2O_2$]$^+$ ($C_{36}H_{78}{}^{63}Cu_2N_6O_2^+$), Δ = 1.5 ppm}, 754.47673 {100.00%, [($^{t}Bu_3tacn$)$_2$$Cu_2O_2$]$^+$ ($C_{36}H_{78}{}^{63}Cu^{65}CuN_6O_2^+$), Δ = 1.7 ppm}, 756.47494 {21.35%, [($^{t}Bu_3tacn$)$_2$$Cu_2O_2$]$^+$ ($C_{36}H_{78}{}^{65}Cu_2N_6O_2^+$), Δ = 1.0 ppm}, 869.44213 {37.84%, [($^{t}Bu_3tacn$)$_2$$Cu_2$(OTf)]$^+$ ($C_{37}H_{78}{}^{63}Cu_2F_3N_6O_3S^+$), Δ = 3.1 ppm}, 871.43957 {37.02%, [($^{t}Bu_3tacn$)$_2$$Cu_2$(OTf)]$^+$ ($C_{37}H_{78}{}^{63}Cu^{65}CuF_3N_6O_3S^+$), Δ = 2.2 ppm}, 873.43693 {7.95%, [($^{t}Bu_3tacn$)$_2$$Cu_2$(OTf)]$^+$ ($C_{37}H_{78}{}^{65}Cu_2F_3N_6O_3S^+$), Δ = 1.2}; negative-mode NSI-MS m/z (relative intensity, formula, ppm) 658.15131 {100.00%, [($^{t}Bu_3tacn$)Cu(OTf)$_2$]$^-$ ($C_{20}H_{39}{}^{63}CuF_6N_3O_6S_2^-$), Δ = 4.1 ppm}, 660.14991 {47.21%, [($^{t}Bu_3tacn$)Cu(OTf)$_2$]$^-$ ($C_{20}H_{78}{}^{65}CuF_6N_3O_2S_2^-$), Δ = 4.7 ppm}. Elemental Anal. Calcd for $C_{38}H_{78}Cu_2F_6N_6O_8S_2$: C, 43.37; H, 7.47; N, 7.99; F, 10.83. Found: C, 43.39; H, 7.33; N, 7.89; F, 11.02.

Aerobic Oxidations. *Oxidation of Benzoin.* With 20 mol % catalyst loading, the procedure is as follows. In a 20 mL glass vial with a stir bar, benzoin (0.02116 g, 99.7 μmol, 1 equiv) and complex **2** (0.02089 g, 19.9 μmol, 19.9 mol %) were dissolved in d_4-methanol (3 mL). Mesitylene (0.01406 g, 117 μmol, 1.2 equiv) was then added as an internal standard. The vial was sealed with an inverted septum and fitted with an O_2 balloon. The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR spectroscopy until the reaction was complete.

With 20 mol % catalyst loading at 50 °C, the procedure is as follows. In a 20 mL glass vial with a stir bar, benzoin (0.02012 g, 94.7 μmol, 1 equiv) and complex **2** (0.02036 g, 19.3 μmol, 20.4 mol %) were dissolved in d_4-methanol (3 mL). Then, 1,3,5-trimethoxybenzene (0.00831 g, 49.4 μmol, 0.52 equiv) was added as an internal standard. The vial was sealed with an inverted septum and fitted with an O_2 balloon. The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR spectroscopy until the reaction was complete.

With 5 mol % catalyst loading, the procedure is as follows. In a 20 mL glass vial with a stir bar, benzoin (0.02145 g, 101 μmol, 1 equiv) and complex **2** (0.00512 g, 4.87 μmol, 4.8 mol %) were dissolved in d_4-methanol. Then, 1,3,5-trimethoxybenzene (0.00587 g, 34.9 μmol, 0.35 equiv) was added as an internal standard. The vial was sealed with an inverted septum. The reaction mixture was stirred at 50 °C open to air and monitored by ^{1}H NMR until the reaction was complete.

Oxidation of 2,4-Di-tert-butylphenol. In a 20 mL glass vial, 2,4-di-*tert*-butylphenol (0.04134 g, 200 μmol, 1 equiv) and 1,3,5-trimethoxybenzene (0.00557 g, 33.1 μmol, 0.17 equiv) were dissolved in d_4-methanol (8 mL) to make a stock solution. Then complex **2** [0.00497 g (room temperature), 4.72 μmol, 18.9 mol %; 0.00531 g (50 °C), 5.07 μmol, 20.1 mol %; 0.00567 g (65 °C), 5.39 μmol, 21.5 mol %] was added to an NMR tube. To each tube with complex **2** was added 1.0 mL of the stock solution. The tubes were capped, fitted with an O_2 balloon, and heated to their respective temperatures. The reactions were monitored by ^{1}H NMR spectroscopy until they were complete.

Oxidation of 3,5-Di-tert-butylcatechol. In a 20 mL glass vial, 3,5-di-*tert*-butylcatechol (0.04100 g, 184 μmol, 1 equiv) and 1,3,5-tri-*tert*-butylbenzene (0.01262 g, 51.2 μmol, 0.28 equiv) were dissolved in d_4-methanol (8 mL) to make a stock solution. Then complex **2** [0.00512 g (room temperature), 4.87 μmol, 21.1 mol %; 0.00560 g (50 °C), 5.32 μmol, 23 mol %; 0.00450 g (65 °C), 4.28 μmol, 18.6 mol %] was added to an NMR tube. To each tube with complex **2** was added 1.0 mL of the stock solution. The tubes were capped, fitted with an O_2 balloon, and heated to their respective temperatures. The reactions were monitored by ^{1}H NMR spectroscopy until they were complete.

Oxidation of Benzyl Alcohol. In a 100 mL volumetric flask, benzyl alcohol (0.01146 g, 106 μmol, 1 equiv) and 1,3,5-tri-*tert*-butylbenzene (0.00726 g, 29.5 μmol, 0.28 equiv) were dissolved in methanol to a volume of 100 mL as a stock solution. To 25 mL three-necked flasks equipped with stir bars and reflux condensers was added complex **2** [0.01028 g (room temperature), 9.77 μmol, 0.92 equiv; 0.01098 g (50 °C), 10.4 μmol, 0.98 equiv; 0.01036 g (65 °C), 9.84 μmol, 0.93 equiv]. To each flask with complex **2** was added 10 mL of the stock solution. Each reaction mixture was fitted with an O_2 balloon atop the condenser, and the reaction mixtures were stirred and heated to their respective temperatures. The reactions were monitored by gas chromatography.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02205.

Crystallographic information files (CIF)

Crystallographic data collection and refinement details, decomposition studies followed by UV−vis spectroscopy, and raw characterization of organic and transition-metal compounds by NMR spectroscopy (PDF)

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Notes

The authors declare no competing financial interest.

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