Aerobic Oxidation Reactivity of Well-Defined Co^{II} and Co^{III} Aminophenol Complexes

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Supporting Information Placeholder

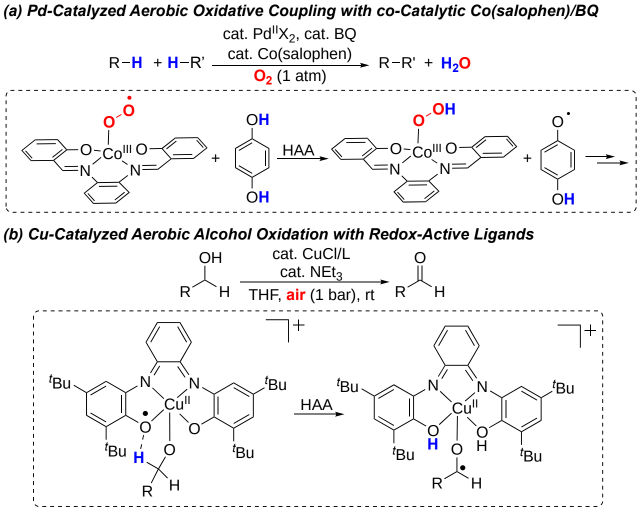
ABSTRACT: This article describes the synthesis and reactivity studies of three cobalt complexes bearing aminophenol-derived ligands without nitrogen substitution: $Co^{II}(^{tBu2}APH)_2(^{tBu2}AP)_2$ (**1**), $Co_2^{III}(^{tBu2}APH)_2(^{tBu2}AP)_2(\mu\text{-}^{tBu2}BAP)_2$ (**2**), and $Co^{III}(^{tBu2}AP)_3$ (**3**) (^{tBu2}APH = 2-amino-4,6-di-*tert*-butylphenol, ^{tBu2}AP = 2-amino-4,6-di-*tert*-butylphenolate, $\mu\text{-}^{tBu2}BAP$ = bridging 2-amido-4,6-di-*tert*-butylphenolate). Stoichiometric reactivity studies of these well-defined complexes demonstrate the catalytic competency of both Co^{II} and Co^{III} complexes in the aerobic oxidative cyclization of ^{tBu2}APH with *tert*-butyl isonitrile. Reactions with O_2 reveal the aerobic oxidation of Co^{II} complex **1** to generate the Co^{III} species **2** and **3**. UV-visible time-course studies and EPR spectroscopy indicate that this oxidation proceeds through a ligand-based radical intermediate. These studies represent the first example of well-defined cobalt-aminophenol complexes that participate in catalytic aerobic oxidation reactions and highlight a key role for a ligand radical in the oxidation sequence.

INTRODUCTION

Cobalt complexes are attractive catalysts for aerobic oxidation reactions due to their well-recognized ability to activate molecular oxygen.[1,2] Catalytic methods have been devised for the aerobic oxygenation of a variety of organic substrates including alkenes,[3] phenols,[4] amines,[5] sulfides[6] and phosphines.[7] These reactions often rely on the inclusion of co-reductants, such as aldehydes or silanes, to achieve efficient turnover. An alternative strategy employs redox-active cofactors, such as NHPI, for the catalytic oxygenation of alkenes and alkanes (NHPI = *N*-hydroxyphthalimide).[8] Under these conditions, a cobalt-peroxo intermediate abstracts a hydrogen atom from NHPI to generate the PINO• radical, which is responsible for generation of the substrate carbon radical (PINO• = phthalimide *N*-oxyl radical). Trapping of this substrate radical with O_2 leads to the oxygenated products. The hydrogen atom abstraction (HAA) behavior of Co/O_2 systems has also been used to enable catalytic oxidase-type reactions. Quinone is commonly employed as a redox co-catalyst paired with Co-salen or -salophen complexes to aid in the efficient utilization of O_2 in aerobic oxidation reactions catalyzed by Pd and Ru.[9] In these systems the Co^{III}-OO• intermediate abstracts a hydrogen atom from hydroquinone to generate the semiquinone intermediate and ultimately the quinone, which serves to re-oxidize the Pd or Ru (Scheme 1a).[10]

A related approach uses redox-active ligands to enable catalytic aerobic oxidation reactions.[11] Inspired by enzymatic systems[12] such as galactose oxidase,[13] catechol dioxygenases,[14] and aminophenol dioxygenases[15] researchers have applied catechol, *ortho*-aminophenol, and *ortho*-phenylenediamine ligands to aerobic oxidation reactions catalyzed by first-row transition metals.[16] For example, Wieghardt and co-workers demonstrated an aerobic alcohol oxidation reaction catalyzed by Cu^{II} and Zn^{II} complexes with tetradentate redox non-innocent aminophenol-derived ligands.[17] The reaction was suggested to proceed via rate-determining C-H HAA of the bound alkoxide by a ligand radical (Scheme 1b). Storr and co-workers have reported a related copper complex bearing a hybrid amidophenol-amidopyridine ligand that enables aerobic oxidation of alcohols via a phenoxyl ligand radical.[18]

Scheme 1. Intermediacy of Phenoxyl Radicals for HAA in Select Aerobic Oxidation Reactions

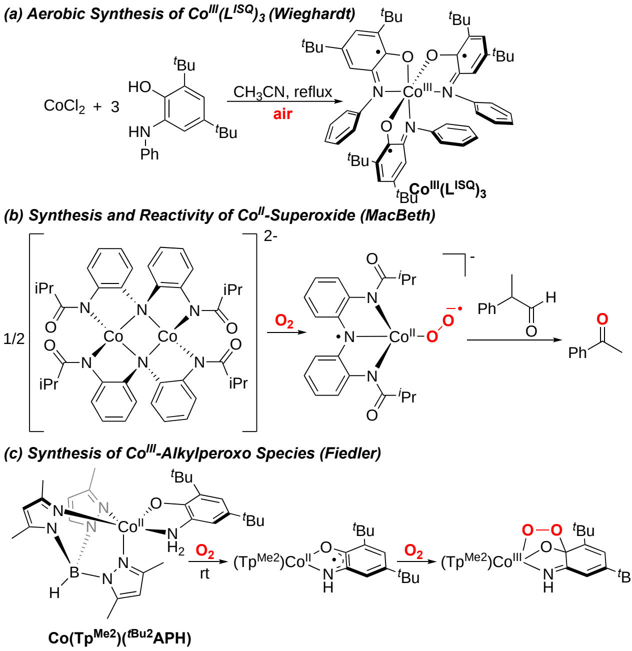


(a) Pd-Catalyzed Aerobic Oxidative Coupling with co-Catalytic Co(salophen)/BQ

(b) Cu-Catalyzed Aerobic Alcohol Oxidation with Redox-Active Ligands

Stochiometric studies of catechol- and aminophenol-ligated Co complexes have supported the possible role of ligand non-innocence in catalytic oxidation reactions.[19-21] Early work by Pierpont and coworkers described the tris(3,6-di-*tert*-butylsemiquinonato)cobalt(III) complex (Co(3,6-DBSQ)) generated upon treatment of $Co_2(CO)_8$ with 3,6-di-*tert*-butyl-1,2-benzoquinone (3,6-DBBQ).[21a] The related *ortho*-aminophenols have been shown to behave with similar redox flexibility, occupying one of three different oxidation states; the dianionic amidophenolate, the monoanionic aminophenolate, or the radical iminosemiquinonato (ISQ) forms. Of particular interest, Weighardt and coworkers reported the amino-phenol derived $Co^{III}(L^{ISQ})_3$ complex (L^{ISQ} = *N*-phenyl-4,6-*tert*-butyl-iminosemiquinonanto) (Scheme 2a).[20a] In this system, aerobic oxidation of the Co^{II} and *N*-phenyl-4,6-di-*tert*-butylaminophenol precursors led to oxidation of both the Co center and the ligand to yield the iminosemiquinonato complex.

Scheme 2. Well-Defined Co Species Isolated from Aerobic Oxidation Reactions.


(a) Aerobic Synthesis of $Co^{III}(L^{ISQ})_3$ (Wieghardt)

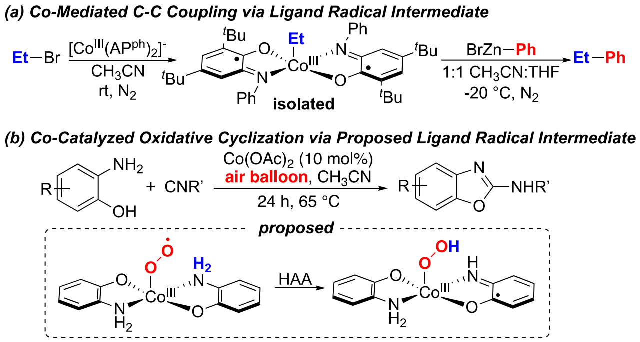
(b) Synthesis and Reactivity of Co^{II}-Superoxide (MacBeth)

(c) Synthesis of Co^{III}-Alkylperoxo Species (Fiedler)

MacBeth and coworkers have reported a bimetallic Co complex bearing the redox-active bis(2-isobutyrylamidophenyl)amine ligand ($HN(o\text{-}PhNHC(O)^iPr)_2$) and shown it to activate O_2 for the catalytic oxygenation of triphenylphosphine and the deformylation of 2-phenylpropionaldehyde via a low-spin Co^{II}-superoxide intermediate (Scheme 2b).[22] In an elegant study, Fiedler and coworkers have isolated a rare example of a cobalt(III)-alkylperoxo species resulting from catecholase-type reactivity of a cobalt-superoxo (Co-OO•$^-$) intermediate (Figure 2c).[23]

Despite the notable advances in the synthesis, characterization, and reactivity studies of Co complexes bearing catechol- and aminophenol-derived ligands, the application of these complexes in catalysis remain limited. To date, the only work demonstrating the reactivity of cobalt-aminophenolate complexes was reported by Soper and co-workers,[24] who described a square planer Co^{III} complex capable of mediating a Negishi-like cross-coupling reaction of an alkyl halide with an organozinc reagent (Scheme 3a). This example, however, is a stoichiometric redox-neutral coupling performed under anaerobic conditions. We are unaware of any examples of catalytic aerobic oxidation reactions employing Co-aminophenol complexes.

Scheme 3. Cobalt-Mediated Coupling Reactions Employing Redox-Active Aminophenol Ligands.


(a) Co-Mediated C-C Coupling via Ligand Radical Intermediate

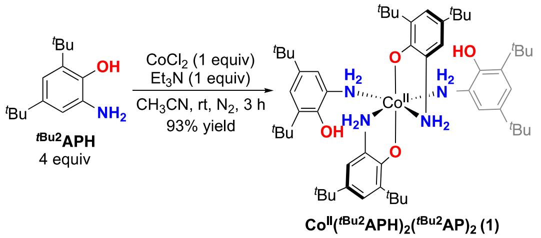
(b) Co-Catalyzed Oxidative Cyclization via Proposed Ligand Radical Intermediate

We recently reported the aerobic oxidative coupling of substituted *ortho*-aminophenols with isonitriles (CNR) and proposed the reaction to proceed through an intermediate in which the aminophenol ligand plays a key role in the O_2 activation step (Scheme 3b).[25] In this work, we disclose three new Co^{II}- and Co^{III}-aminophenol complexes and demonstrate that both Co^{II} and Co^{III} complexes are catalytically active in this aerobic coupling reaction. The stoichiometric reactivity of these species supports O_2 activation by Co^{II} to generate an aminophenol-ligand radical, which then undergoes coupling with isonitrile (CNR).

RESULTS AND DISCUSSION

Synthesis and Characterization of $Co^{II}(^{tBu2}APH)_2(^{tBu2}AP)_2$ (1). We first targeted the Co species bearing the unsubstituted *ortho*-aminophenol ligand; however, attempts to isolate this complex resulted in product mixtures. Instead, 2-amino-4,6-di-*tert*-butyl phenol (^{tBu2}APH) was used for the synthesis of the well-defined cobalt complexes. The Co^{II} complex $Co^{II}(^{tBu2}APH)_2(^{tBu2}AP)_2$ (**1**) was synthesized from $CoCl_2$ and ^{tBu2}APH in the presence of triethylamine (Et_3N) in acetonitrile under an inert atmosphere (Scheme 4). $CoCl_2$ was chosen as the cobalt source for its greater solubility compared to $Co(OAc)_2$, which was employed under the original catalytic oxidative cyclization conditions. Complex **1** was obtained in the highest yield (93%) when a 1:4 metal to ligand ratio was employed, however **1** was also formed as the predominant Co species when M:L ratios of 1:1, 1:2 and 1:3 were used (Table S1).

Scheme 4. Synthesis of $Co^{II}(^{tBu2}APH)_2(^{tBu2}AP)_2$ (1).



The paramagnetic Co^{II} complex **1** was characterized by elemental analysis, X-ray crystallography, NMR and absorption spectroscopies as well as cyclic voltammetry. The 1:4 metal to ligand ratio of the isolated compound was confirmed by combustion analysis and X-ray crystallography. Light green-yellow single crystals suitable for X-ray diffraction were obtained by slow evaporation of the reaction solvent under anaerobic conditions. The solid-state structure contains a mononuclear Co^{II} center in a distorted octahedral geometry. Co is bound by two monodentate aminophenol ligands (^{tBu2}APH) oriented *cis* to one another and two bidentate aminophenolate ligands (^{tBu2}AP, Figure 1). The bond lengths and angles show no evidence of a quinoidal-type distortion and point toward aromatic ^{tBu2}AP ligands. The aromaticity of the ligands is supported by the electronic spectrum of complex **1**, which displays an absorption maximum in the UV region (λ_{max} = 381 nm, $\varepsilon = 0.8\times10^4$ $M^{-1}cm^{-1}$, Figure S7), characteristic of aromatic aminophenol ligands.[26] The paramagnetic nature of complex **1** is evident from NMR spectroscopy. The ^{1}H NMR spectrum of compound **1** features two broad peaks around 30 ppm and 50 ppm (Figure S1), while the magnetic susceptibility of the complex (μ_{eff} = 4.04 μ_B) indicates a high spin S=3/2 Co center.[27]

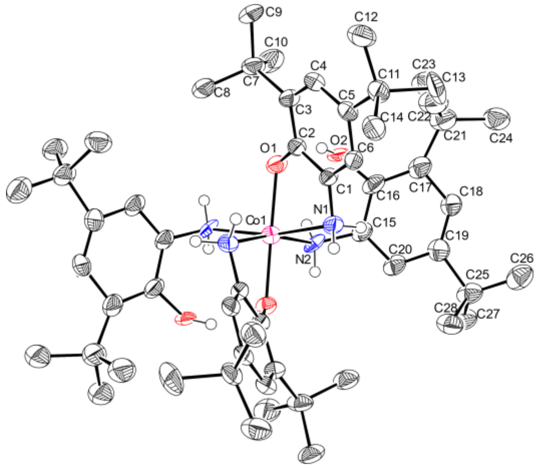


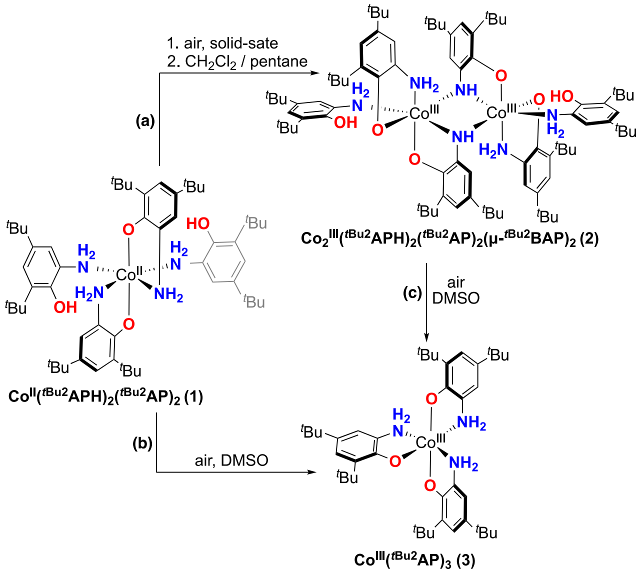
Figure 1. The structure of $Co^{II}(^{tBu2}APH)_2(^{tBu2}AP)_2$ (**1**). All non-hydrogen atoms are drawn at 50% thermal probability ellipsoids. All hydrogen atoms except those on heteroatoms are omitted for clarity. Selected bond distances (Å): Co1-N1 2.162(3), Co1-N2 2.231(15), Co1-O1 1.986(3), O1-C2 1.330(5), N1-C1 1.415(14), C1-C2 1.396(6), C2-C3 1.405(6), C3-C4 1.368(6), C4-C5 1.371(7), C5-C6 1.365(6).

The observed formation of complex **1** regardless of the Co:L ratio contrasts literature reports in which the 1:3[20b] and 1:2 complexes are isolated.[20d] Furthermore, prior examples of Co-AP complexes include bulky substituents on the nitrogen of the AP ligand.[20d,e] This substitution likely stabilizes the 1:2 and 1:3 coordination complexes. Complex **1**, as well as complexes **2** and **3** (vide infra), are the first examples of isolable Co complexes ligated by only aminophenol-derived ligands which bear a free NH_2 group. The *tert*-butyl groups on the aromatic ring, however, are crucial to obtain a stable and isolable Co^{II} complex.

Oxidation of Complex 1. Wieghardt and coworkers have shown the Co^{II} complex bearing 2-amino-4,6-di-*tert*-butyl thiophenol ligands to undergo solid-state oxidation upon exposure to air.[20d] We sought to explore the corresponding oxidation of complex **1**. The electrochemical oxidation of **1** was measured via cyclic voltammetry in DMSO. The resulting voltammogram displayed a single quasi-reversible redox event at $E_{1/2}$ = 0.145 V versus Fc/Fc^+ (Figure S8). This redox potential suggests that the aerobic oxidation of complex **1** should be thermodynamically feasible.[28]

The aerobic oxidation of complex **1** was probed by ^{1}H NMR spectroscopy. Introduction of a headspace of air into a solution of **1** in C_6D_6 led to the rapid formation of a diamagnetic species (within 5 min), followed by its slow decomposition over an extended period of time (hours). The resulting diamagnetic Co^{III} species was determined to be the dinuclear complex $Co_2^{III}(^{tBu2}APH)_2(^{tBu2}AP)_2(\mu\text{-}^{tBu2}BAP)_2$ (**2**) (Scheme 5a) following the independent synthesis from the solid-state air oxidation of **1**, described below. Conducting the analogous aerobic oxidation of **1** in DMSO led instead to the formation of the mononuclear Co^{III} complex $Co^{III}(^{tBu2}AP)_3$ (**3**) (Scheme 5b). Complex **3** was also obtained from the continued conversion of dimeric **2** in situ in DMSO. The syntheses, characterization and reactivity studies of **2** and **3** are described below.

Scheme 5. Syntheses of $Co_2^{III}(^{tBu2}APH)_2(^{tBu2}AP)_2(\mu\text{-}^{tBu2}BAP)_2$ (2) and $Co^{III}(^{tBu2}AP)_3$ (3).



Synthesis and Characterization of $Co_2^{III}(^{tBu2}APH)_2(^{tBu2}AP)_2(\mu\text{-}^{tBu2}BAP)_2$ (2). Upon exposure of solid **1** to air, a color change from light grey to the shiny dark violet color of **2** was observed. Plate-shaped single crystals were obtained by slow diffusion of pentane into a concentrated solution of **2** in CH_2Cl_2 under an anaerobic atmosphere. The X-ray crystal structure reveals a dimeric complex in which each cobalt center is ligated by three aminophenol-derived ligands with distinct coordination modes (Figure 2). Each Co center bears a neutral aminophenol ligand (^{tBu2}APH), a monoanionic aminophenolate ligand (^{tBu2}AP), and a bridging amidophenolate ligand (μ-^{tBu2}BAP) connecting the two cobalt centers via the NH group. The Co-N bond lengths for the bidentate and bridging aminophenol ligands are similar with values of 1.9373(15) Å and 1.9172(14) Å, respectively. Both distances are shorter than the Co-N bond distance of the monodentate aminophenol ligand (2.0524(15) Å). The Co-O bond lengths for the bidentate and bridging ligands are also similar with lengths of 1.9176(12) Å and 1.9104(12) Å, respectively. Both bond lengths are significantly longer than those measured for the related tris(*o*-iminosemiquinone) cobalt(III) complex (1.8784(9) – 1.8960(9) Å).[20a] The bond lengths of complex **2** revealed no significant elongation or shortening of C-N and C-O bonds, suggesting aromatic aminophenol ligands and the absence of ligand radicals in this cobalt complex.[20b]

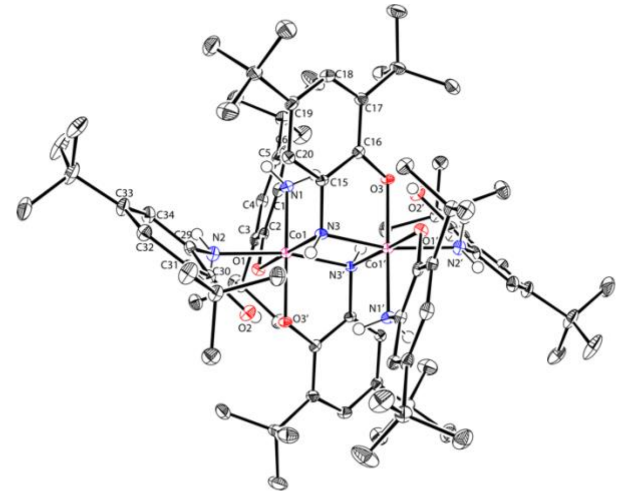


Figure 2. The ORTEP structure of $\mathrm{Co_2^{III}}(^{t\mathrm{Bu2}}\mathrm{APH})_2(^{t\mathrm{Bu2}}\mathrm{AP})_2(\mu\text{-}^{t\mathrm{Bu2}}\mathrm{BAP})_2$ (**2**). All non-hydrogen atoms are drawn at 50% thermal probability ellipsoids. All hydrogen atoms except those on heteroatoms are omitted for clarity. Selected bond distances (Å): Co1-N1 1.9373(15), Co1-N2 2.0524, Co1-N3 1.9172(14), Co1-O1 1.9176(12), Co1-O3 1.9104(12), O1-C2 1.331(2), O2-C30 1.365(2), O3-C16 1.362(2), N1-C1 1.458(2), N2-C29 1.454(2), N3-C15 1.441(2).

The ^{1}H NMR spectrum of the crystals of **2** dissolved in $\mathrm{C_6D_6}$ under an anaerobic atmosphere revealed a diamagnetic Co species with a 1:3 metal to ligand ratio, in good agreement with the single crystal data (Figure 3). The spectrum features six distinct signals in the aromatic region as well as six different ^{t}Bu resonances between 1.3-1.5 ppm. Six broad peaks were also observed between 2.5-5.5 ppm, and deuteration with $\mathrm{D_2O}$ / MeOD confirmed these to be exchangeable N*H* and O*H* protons (Figures 3 and S4). Absorption spectroscopy of **2** measured in $\mathrm{CH_2Cl_2}$ presented two broad bands around 520 nm ($\varepsilon = 5.8\times10^2$ $\mathrm{M^{-1}\,cm^{-1}}$) and 580 nm ($\varepsilon = 5.8\times10^2$ $\mathrm{M^{-1}\,cm^{-1}}$), assigned as charge transfer bands (Figure S7).

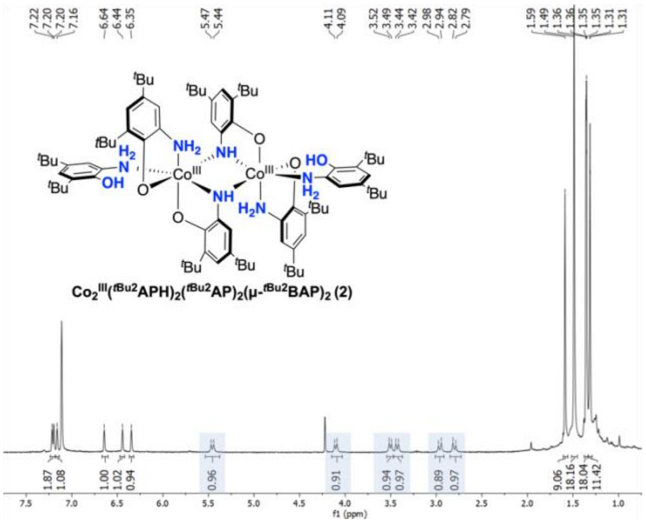


Figure 3. ^{1}H NMR spectrum of $\mathrm{Co_2^{III}}(^{t\mathrm{Bu2}}\mathrm{APH})_2(^{t\mathrm{Bu2}}\mathrm{AP})_2(\mu\text{-}^{t\mathrm{Bu2}}\mathrm{BAP})_2$ (**2**) in $\mathrm{C_6D_6}$ with the signals resulting from exchangeable N*H* and O*H* protons highlighted in blue.

Synthesis and Characterization of $\mathbf{Co^{III}}(^{t\mathrm{Bu2}}\mathbf{AP})_3$ (3). The batch isolation of the monomeric $\mathrm{Co^{III}}(^{t\mathrm{Bu2}}\mathrm{AP})_3$ complex (**3**) was achieved by slow oxidation of the low-valent complex **1** in DMSO under an air atmosphere (Scheme 5b). The limited solubility of **3** drives the oxidation towards a single species allowing for the selective conversion to **3**. Dark violet single crystals suitable for X-ray diffraction were formed during the oxidation. Structural analysis revealed a Co center coordinated by three aminophenolate ($^{t\mathrm{Bu2}}$AP) ligands in a distorted octahedral geometry (Figure 4). The three $^{t\mathrm{Bu2}}$AP ligands each exist in a unique coordination environment giving the structure overall C_1 symmetry. The Co-O (1.8851(12), 1.9012(12) and 1.9047(12) Å) bond lengths are significantly shorter than those measured for the aminophenolate ligand of $\mathrm{Co(Tp^{R2})}(^{t\mathrm{Bu2}}\mathrm{APH})$ (R = Ph, Co-O = 1.9301(17) Å; R = Me Co-O = 1.9766(10) Å),[23] likely due to the higher oxidation state of the $\mathrm{Co^{III}}$ center. The Co-N (1.9394(14), 1.9623(14), and 1.9451(14) Å) bond lengths are also significantly shorter than those measured in the same complexes (R = Ph, Co-N = 2.154(2) Å; R = Me, Co-N = 2.1292(13) Å). The related tris(*o*-iminosemiquinone) cobalt(III) complex reported by Weighardt and coworkers[20a] contains Co-O and Co-N bonds (Co-O = 1.878(1) - 1.896(1) Å, Co-N = 1.918(1) - 1.946(1) Å) that are similar to those of **3**. The aromatic C-C bond distances of **3** (1.377(2) Å - 1.424(2) Å) are similar to those calculated for the neutral aminophenol ligand (1.38-1.41 Å)[29] and indicate the absence of ligand radical character. Complex **3** was further characterized by combustion analysis and NMR and UV-visible spectroscopies.

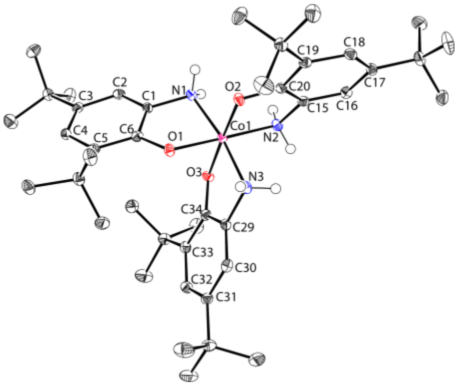


Figure 4. The ORTEP structure of $\mathrm{Co^{III}}(^{t\mathrm{Bu2}}\mathrm{AP})_3$ (**3**). All non-hydrogen atoms are drawn as 50% thermal probability ellipsoids. Solvent molecules and all hydrogen atoms except those on heteroatoms are omitted for clarity. Selected bond distances (Å): Co1-N1 1.9394(14), Co1-N2 1.9623(14), Co1-N3:1.9451(14), Co1-O1 1.8851(12), Co1-O2 1.9012(12), Co1-O3 1.9047(12), C1-N1 1.460(2), C15-N2 1.461(2), C29-N3 1.459(2), C6-O1 1.332(2), C20-O2 1.330(2), C34-O3 1.335(2), C1-C2 1.377(2), C2-C3 1.400(2), C3-C4 1.398(2), C4-C5 1.401(2), C5-C6 1.410(2), C1-C6 1.401(2).

Intermediacy of a Ligand Radical. The generation of $\mathrm{Co^{III}}$ species **2** and **3** from the aerobic oxidation of the low valent complex **1** indicates the ability of $\mathrm{Co^{II}}$ complex **1** to activate $\mathrm{O_2}$. In related systems, $\mathrm{Co^{II}}$ has been shown to activate $\mathrm{O_2}$ to yield $\mathrm{Co^{III}}$-peroxide,[30] -alkylperoxo or superoxo intermediates.[23] The possible formation of radical intermediates in the aerobic oxidation of **1**, was probed with EPR spectroscopy. A solution of complex **1** in $\mathrm{CH_2Cl_2}$ under $\mathrm{N_2}$ was exposed to air for 5 seconds and then frozen. The spectrum of the frozen solution showed an 8-line pattern characteristic of an $S = 1/2$ system with coupling of a single electron to the ^{59}Co center ($I = 7/2$) and A values indicative of a ligand-centered spin (Figure 5). These data suggested the formation of a low-spin $\mathrm{Co^{III}}$ ligated by either an aminophenol-centered radical or a superoxide radical.

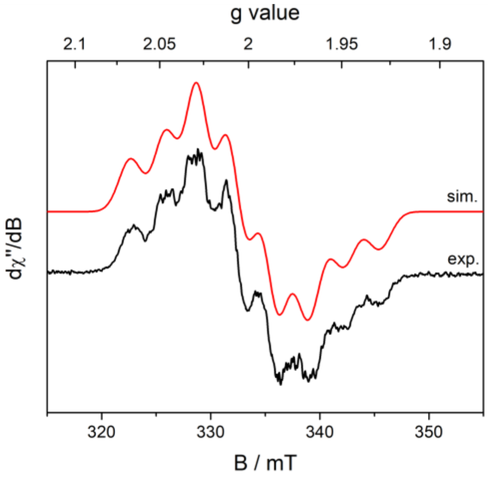


Figure 5. Experimental EPR data and simulation for $Co^{II}(^{tBu2}APH)_2(^{tBu2}AP)_2$ (**1**) after exposure to air. Conditions: 1 mM complex **1** in CH_2Cl_2. The sample was prepared inside a N_2 filled glovebox and the spectrum was taken immediately after the sample was exposed to air then frozen in liquid N_2. Spectrum measured at 77 K. Final fit parameters: g(z) = 2.013, g(y) = 1.996, g(x) = 1.989; A(zz) = 21.5 MHz, A(yy) = 90.9 MHz, A(xx) = 21.8 MHz (coupling to ^{59}Co, I = 7/2, 100% natural abundance).

A cobalt-superoxide intermediate is expected to be very short-lived and likely to undergo a rapid intramolecular hydrogen-atom transfer to generate a ligand phenoxyl radical coupled to a low spin Co^{III} center (Scheme 3b). The hyperfine coupling constants measured in the oxidation of **1** with O_2 are in a good agreement with the reported Co^{III} salen species in which the ligand phenoxyl radical is coupled to the cobalt center.[31] Our results combined with the literature precedent indicate that a phenoxyl radical or a delocalized carbon-centered ligand radical may exist in our system as a result of O_2 activation.

The possible involvement of an aminophenol ligand radical was further probed by UV-visible spectroscopy. Introduction of air into a solution of **1** in THF at -78 °C showed no spectroscopic changes (Figure S12). At room temperature in CH_2Cl_2, however, treatment of **1** with air resulted in the rapid generation of three bands around 530, 650 and 860 nm consistent with ligand to metal charge transfer (LMCT) bands of a Co^{III} complex (Figure 6). In particular, bands around 800 nm have been attributed to ligand-radicals in related systems.[23,31] The apparent formation of a ligand radical species paired with the lack of an observable $Co^{III}OO$• intermediate, even at low temperatures, suggests a very rapid hydrogen atom transfer (HAT) process, possibly due to the intramolecular nature of the transfer.

In further support of this assignment, treatment of complex **1** with the 2,4,6-tri-*tert*-butylphenoxyl radical, a hydrogen atom abstraction reagent,[12,33] leads to the formation of the same spectroscopic signatures, suggesting formation of the same ^{tBu2}AP radical intermediate (Figure 6). This intermediate is not stable over prolonged periods and the corresponding signals disappear when the solution is left to react under an aerobic atmosphere overnight.

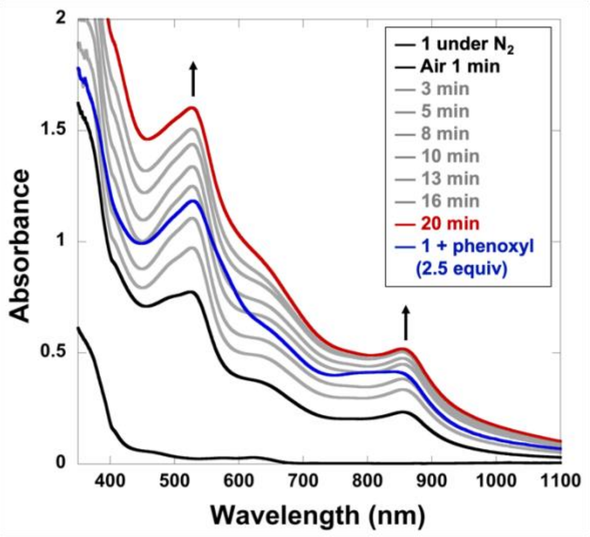
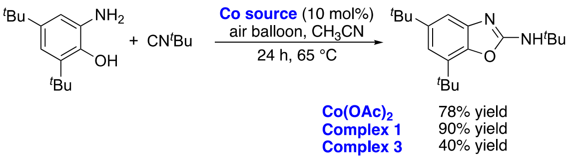


Figure 6. Air oxidation of $Co^{II}(^{tBu2}APH)_2(^{tBu2}AP)_2$ (**1**) monitored by UV-Visible spectroscopy. Conditions: $5{\times}10^{-4}$M in CH_2Cl_2. The sample was monitored for 3 hours following the exposure to air. The first 20 min are included here.

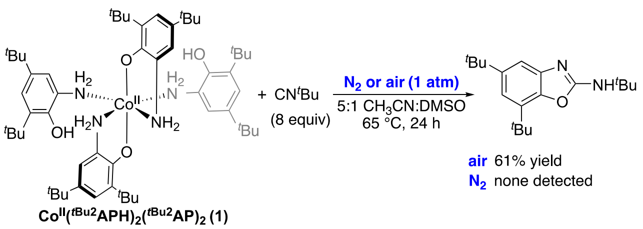
Coupling Reactivities of Complexes 1 and 3. Prior to exploring the reactivities of the well-defined Co complexes in the aerobic coupling with isonitriles, ^{tBu2}APH was first confirmed to undergo efficient coupling under the standard reaction conditions. Treatment of ^{tBu2}APH with *tert*-butylisonitrile (CN*t*Bu) in the presence of catalytic $Co(OAc)_2$ in MeCN under air led to the generation of the corresponding 2-*tert*-butylaminobenzoxazole in 78% yield (Scheme 6). Employing the Co^{II} complex **1** as the catalyst led to high yields of the product (90%), while the Co^{III} complex **3** provided only 40% yield (Scheme 6). Given the disparity in yields, we further explored the reactivity of both complexes under stoichiometric reaction conditions.

Scheme 6. Cobalt-Catalyzed Oxidative Coupling of ^{tBu2}APH with *tert*-Butylisonitrile.



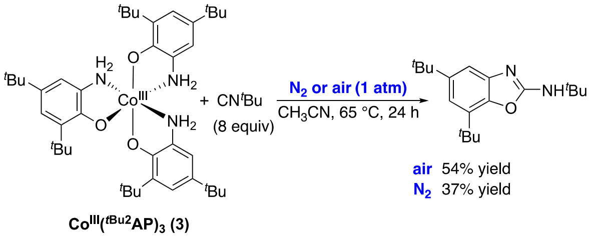
The stoichiometric competencies of complexes **1** and **3** were tested with the addition of CN*t*Bu under both aerobic and anerobic reaction conditions (Scheme 7). In the case of Co^{II} complex **1**, no benzoxazole product was observed under a N_2 atmosphere, while 61% yield was obtained when the reaction was conducted under air. These data indicate the need for an oxidant when Co^{II} species are employed.

Scheme 7. Stoichiometric Control Experiments of $Co^{II}(^{tBu2}APH)_2(^{tBu2}AP)_2$ (1) under Aerobic and Anaerobic Reaction Conditions.



The analogous reactions employing the Co^{III} complex **3** led to the formation of benzoxazole under both anaerobic (37%) and aerobic (54%) conditions, with a higher yield obtained under the latter (Scheme 8). These results suggest that Co^{III} is capable of mediating the oxidative cyclization in the absence of an external oxidant. The lower yield, however, may indicate an alternative reaction pathway is operative. Reduced yields by Co^{III} under N_2 indicate the importance of Co^{II}/O_2 in accessing an active intermediate other than Co^{III}. Thus, our further studies have focused on the aerobic oxidation pathway from Co^{II}.

Scheme 8. Stoichiometric Control Experiments of $Co^{III}(^{tBu2}AP)_3$ (3) under Aerobic and Anaerobic Reaction Conditions.



Product formation from complex **1** could occur directly at the bound ^{tBu}AP ligand or with the free APH through an outer-sphere pathway. To probe if product forms more readily from the bound ^{tBu}AP or free APH, the crossover experiment was conducted with the unsubstituted aminophenol under our standard oxidative cyclization conditions. Treatment of the well-defined Co^{II} complex **1** with the parent APH and CN^{t}Bu leads to the formation of both possible coupling products resulting from coupling of free APH and ligand ^{tBu2}AP in 55% and 32% yields respectively (Figure 7). Similarly, treatment of Co^{III} complex **3** with APH and CN^{t}Bu also forms both possible benzoxazole products in 50% and 29% yields respectively (Figures S18 and S19).

The majority of the ^{tBu2}AP ligand is converted to product. To determine if this conversion of ligand occurs more rapidly or more slowly than reaction of the free APH, the formation of the two different benzoxazole products was monitored over time by ^{1}H NMR spectroscopy (Figure 7A). Early reaction times showed an initial burst in formation of the 5,7-di-*tert*-butyl-2-(*tert*-butylamino)benzoxazole, with saturation occurring after approximately 1 hour (Figure 7B). The formation of the unsubstituted 2-(*tert*-butylamino)benzoxazole derived from free APH occurred with a linear increase during the first 6 h of the reaction. These data suggest that product formation occurs more rapidly at the bound ^{tBu2}AP and that the unsubstituted APH is activated by coordination following the dissociation of product. Thus, these results support a ligand-based oxidative coupling reaction that occurs at the Co-center, and do not support an outer-sphere electron-transfer type pathway.

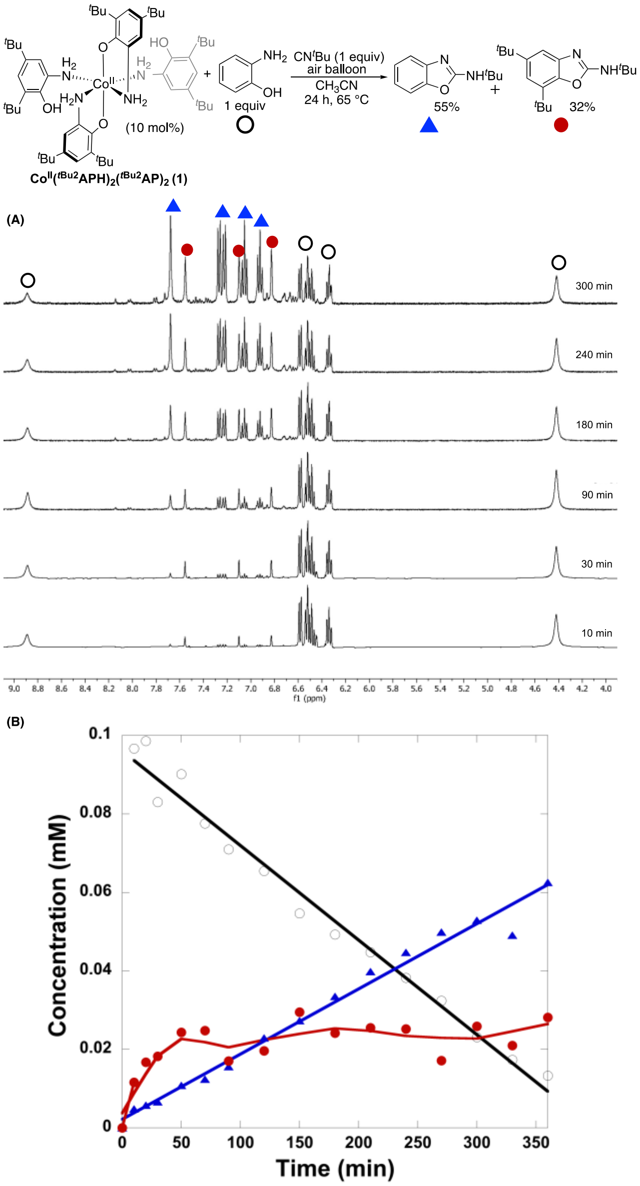
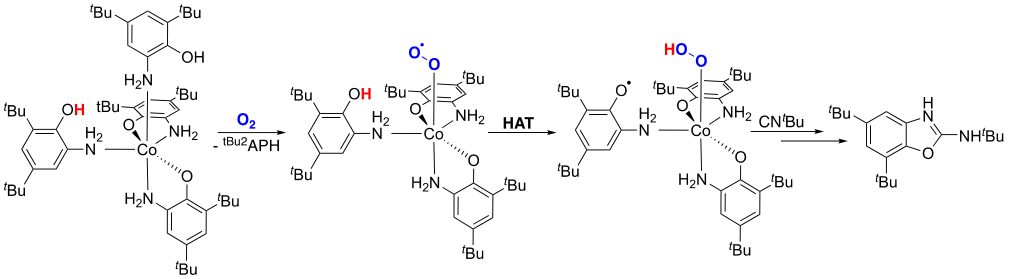


Figure 7. (A) ^{1}H NMR spectra and (B) reaction time-course plot for the reaction of $Co^{II}(^{tBu2}APH)_2(^{tBu2}AP)_2$ **(1)** with 2-aminophenol (APH) and *tert*-butyl isocyanide (CN^{t}Bu). Open circles (○) indicate aminophenol, blue triangles (▲) indicate 2-(*tert*-butylamino)benzoxazole; and red circles (●) indicate 5,7-di-*tert*-butyl-2-(*tert*-butylamino)benzoxazole. Initial conditions: 2-aminophenol (0.5 mmol in 5 mL CH_3CN), *tert*-butyl isocyanide (0.5 mmol in 5 mL CH_3CN), Complex **1** (0.05 mmol in 5 mL CH_3CN).

Scheme 9. Putative Pathway for the Formation of 2-(*tert*-Butylamino)benzoxazole from Complex 1 in the Presence of O_2 and *tert*-Butylisonitrile.



Overall, the data reported here support the intermediacy of an ^{tBu2}AP ligand radical that is formed from the aerobic oxidation of Co^{II} (**1**). Crossover experiments of complex **1** with the parent APH indicate that the reaction occurs more rapidly at the metal center with ligated ^{tBu2}AP than with unbound APH. Coordination of O_2 to **1** would generate a Co-O_2• species which undergoes rapid intramolecular HAA to yield the ligand ^{tBu2}AP radical observed by EPR and UV-visible spectroscopies. The resulting ligand radical is then trapped with CN^{t}Bu to ultimately generate the benzoxazole product.

CONCLUSION

In this study, we have synthesized and characterized three new cobalt complexes bearing *ortho*-aminophenol-derived ligands. These compounds are the first examples of well-defined cobalt complexes that bear *ortho*-aminophenol ligands with unsubstituted NH_2 groups. Stoichiometric reactivity studies of both Co^{II} and Co^{III} complexes demonstrated both species to mediate the oxidative cyclization reactions of the aminophenol ligand with *tert*-butylisonitrile. Stoichiometric oxidation studies suggested activation of O_2 by the Co^{II} complex **1** to generate a ligand radical intermediate which is trapped by CN*t*Bu.

These studies represent the first example of the reactivity of cobalt-aminophenol complexes in aerobic oxidation catalysis, and highlight a key role for a ligand radical in the oxidation sequence. While extensive stoichiometric studies of related cobalt-aminophenol complexes have been reported, prior systems all bear bulky substituents on the nitrogen and are not catalytically relevant. We anticipate that these new unsubstituted analogs will prove valuable to the study of other Co-catalyzed aerobic oxidation reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Synthetic and catalytic experimental details, complete characterization data for all new compounds (PDF)
Crystallographic data for **1** (CIF)
Crystallographic data for **2** (CIF)
Crystallographic data for **3** (CIF)

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Notes

The authors declare no competing financial interest.

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