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# Isolation of a Terminal Co(III)-Oxo Complex

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Supporting Information

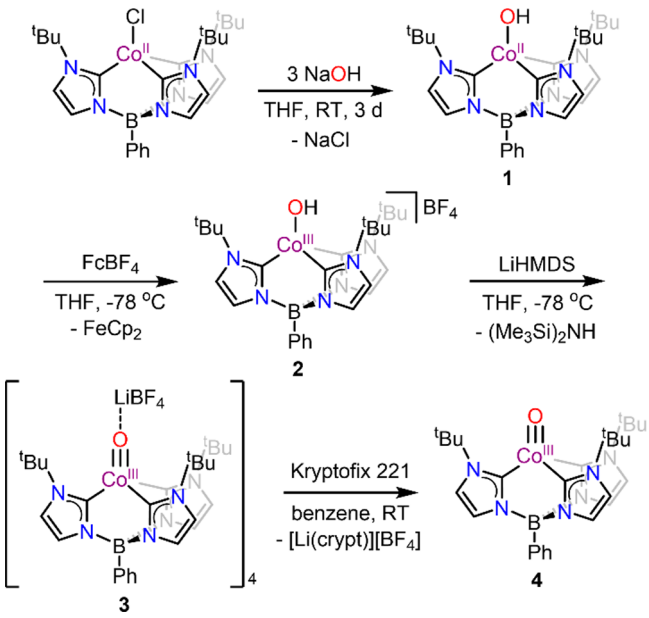
**ABSTRACT:** Late transition metal oxo complexes with high d-electron counts have been implicated as intermediates in a wide variety of important catalytic reactions; however, their reactive nature has often significantly limited their study. While some examples of these species have been isolated and characterized, complexes with d-electron counts >4 are exceedingly rare. Here we report that use of a strongly donating tris(imidazol-2-ylidene)borate scaffold enables the isolation of two highly unusual $Co^{III}$-oxo complexes which have been thoroughly characterized by a suite of physical techniques including single crystal X-ray diffraction. These complexes display O atom and H atom transfer reactivity and demonstrate that terminal metal oxo complexes with six d-electrons can display strong metal−oxygen bonding and sufficient stability to enable their characterization. The unambiguous assignment of these complexes supports the viability of related species that are frequently invoked, but rarely observed, in the types of catalytic reactions mentioned above. The studies described here change our understanding of the reactivity and bonding in late transition metal oxo complexes and open the door to further study of the properties of this class of elusive and important intermediates.

Transition metal oxo complexes have been proposed as intermediates in a variety of important catalytic reactions. For example, these species have been invoked in biological oxidations such as the degradation of pharmaceuticals by cytochrome P450 enzymes and the formation of oxygen from water during photosynthesis.[1,2] Metal oxo intermediates are also cited in synthetic systems such as cobalt oxide catalyzed water oxidation and catalytic epoxidations.[3,4] The ubiquity of transition metal oxo complexes in these reactions has motivated synthetic studies to probe their reactivity and plausibility as intermediates. While many examples of terminal oxo complexes have been studied,[5−8] classic bonding theory and experiment suggests that examples with d-electron counts >4 have weakened metal−oxygen bonds making them highly reactive.[9,10] Indeed, only a handful of such species have been reported to date, with many displaying weak metal−oxygen bonding and instability that has limited their characterization.[11−18]

Complexes with six d-electrons are exceptionally difficult to isolate and have been mischaracterized in some cases.[16] A $Re^{I}$ complex utilizing $\pi$-accepting acetylene ligands and a $Pt^{IV}$ complex with limited structural information remain the sole examples.[17,18] A strategy which should allow for the isolation of multiply bonded, high d-electron count complexes is the use of lower coordinate geometries.[19−25] For example, pseudotetrahedral geometries can stabilize M−L multiple bonds with late transition metals as evidenced by several examples of M−N multiply bonded species.[26−32] Nevertheless, outside of Wilkinson's $d^4$ Ir oxo complex reported 25 years ago,[33] efforts to generate related late transition metal oxo species in pseudotetrahedral ligand environments have proven unsuccessful, as exemplified with tris(pyrazolyl)borate ligands.[6] We rationalized that the stronger carbene donors of the tris(imidazol-2-ylidene)borate ligand $PhB(^{t}BuIm)_3^{-}$ recently employed by Smith and co-workers might enable isolation of a $d^6$ terminal oxo complex.[12,34]

We found that treatment of $PhB(^{t}BuIm)_3Co^{II}Cl$ with NaOH in THF generates a new species, $PhB(^{t}BuIm)_3Co^{II}OH$ (**1**, Scheme 1).[35] Complex **1** has been characterized by a suite of spectroscopic techniques including X-ray diffraction (XRD) that confirm the assignment of a terminal, pseudotetrahedral, $S = 3/2$ $Co^{II}$ hydroxide complex with a Co−O bond length of 1.876(2) Å (Figure 1, Figures S1−S6). This bond length is comparable to other pseudotetrahedral $Co^{II}$-hydroxide complexes.[36,37] Cyclic voltammetry of **1** in MeCN shows a quasi-

**Scheme 1. Synthesis of Complexes 1−4**

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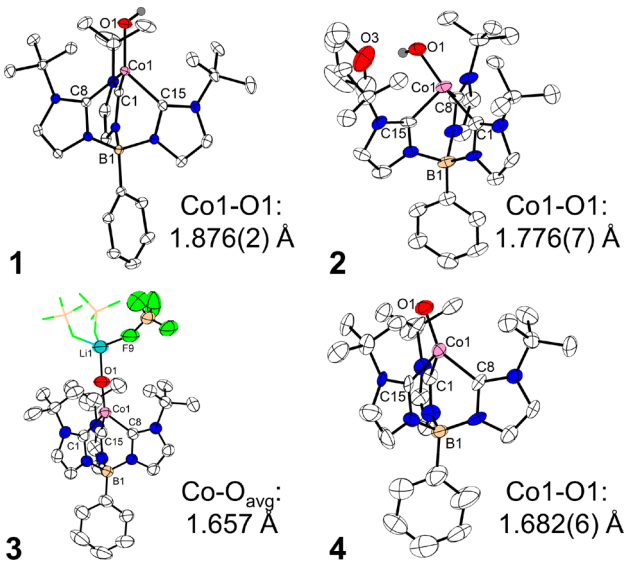


**Figure 1.** Crystal structures of complexes **1**−**4**. Thermal ellipsoids are shown at 50% probability. All H atoms besides those bound to O are omitted for clarity. Counterions and solvent molecules except for the THF in **2** are also omitted. Only one unit of tetrameric **3** is shown with two of the $BF_4^-$ counteranions interacting with the $Li^+$ shown in wireframe. The complete structure is shown in Figure S16.

reversible couple at −230 mV vs Fc/Fc$^+$ (Fc = ferrocene) which is assigned to the Co$^{II}$/Co$^{III}$ redox couple and suggests a Co$^{III}$−OH species may be chemically accessible (Figure S7). Monitoring the addition of 1 equiv of [Fc][$BF_4$] to **1** in THF at −78 °C by UV−vis spectroscopy shows an isosbestic conversion from violet **1** to a green species assigned as the one-electron oxidized product, [PhB($^t$BuIm)$_3$Co$^{III}$OH][$BF_4$] (**2**, Figure S8). This oxidation is also reversible as addition of cobaltocene to *in situ* generated **2** cleanly regenerates **1** (Figure S9).

While **2** is thermally unstable, it is long-lived enough at temperatures <−35 °C to allow for isolation and characterization. Accordingly, single crystals of **2** were obtained at low temperature and the structure reveals a monomeric Co$^{III}$−OH complex in a highly distorted, near seesaw geometry. This distorted geometry may be due to a hydrogen bonding interaction with a THF molecule present in the unit cell, but may also have electronic origins.[38] The Co−O bond length in **2** has contracted by ∼0.1 Å from that in **1** to 1.776(7) Å (Figure 1, Table S1), which is comparable to another four-coordinate Co$^{III}$−OH complex.[39] Complex **2** is diamagnetic, and its NMR features demonstrate that this complex is $C_3$ symmetric in solution (Figures S10−S13).

Using **2** as a synthon, we found that treatment with strong bases such as LiHMDS (HMDS = hexamethyldisilazide) results in generation of a new magenta species (**3**, Figure S14). The reversibility of this reaction by addition of [HNEt$_3$][$BF_4$] suggested the new species may be a Co-oxo complex (Figure S15). Analysis of single crystals grown at −35 °C by XRD reveals a tetrameric species with four PhB($^t$BuIm)$_3$Co$^{III}$O units each capped by a $Li^+$ ion and bridged by $BF_4^-$ anions to give a monomeric formula of PhB($^t$BuIm)$_3$Co$^{III}$O·LiBF$_4$ (Figure 1, Figure S16). In this structure, the average Co−O bond length has shortened by an additional ∼0.1 Å to 1.657 Å, consistent with deprotonation and an increase in formal bond order. In contrast to **2**, the B−Co−O angle is nearly linear at 170.1°. Additionally, isotopically labeled **3** was synthesized from **1**-$^{18}$O and comparison of the IR spectra of **3**-$^{16}$O and **3**-$^{18}$O shows one isotope dependent feature at 839 cm$^{-1}$ which shifts to 802 cm$^{-1}$ upon $^{18}$O incorporation, as expected for a simple harmonic oscillator (Figure 2A, Figure S17A). Finally, **3** is

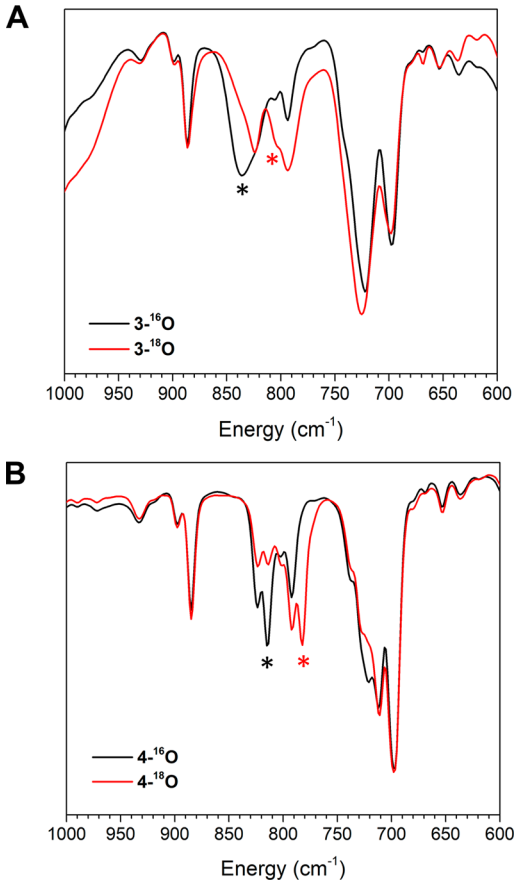


**Figure 2.** Overlay of IR spectra of $^{18}$O-labeled and natural abundance (A) **3** and (B) **4**. Asterisks indicate the feature assigned to the Co−O stretching frequency and its corresponding shift in the $^{18}$O-labeled compound. Difference spectra are shown in Figure S17.

diamagnetic and displays solvent-dependent speciation by NMR spectroscopy in deuterated benzene, THF, and MeCN (Figures S18−S22). This suggested to us that the [Li][$BF_4$] units in **3** could be separated to isolate a bona fide terminal oxo complex.

Addition of Kryptofix 2,2,1 (4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane, crypt) to a benzene solution of **3** results in formation of a purple solution of PhB($^t$BuIm)$_3$Co$^{III}$O (**4**) and precipitation of [Li(crypt)][$BF_4$]. The successful removal of $Li^+$ was confirmed by the loss of signal by $^7$Li NMR spectroscopy. We also note that addition of KHMDS to *in situ* generated **2** results in formation of **4** directly (see Supporting Information). Furthermore, XRD analysis of single crystals of **4** verifies a monomeric complex and shows a Co−O bond length of 1.682(6) Å (Figure 1). There is also a change in the B−Co−O angle upon $Li^+$ sequestration from an average of 170.1° in **3** to 160.2(3)° in **4** giving a slight but noticeably bent structure in the solid state (Table S1). However, similar to complexes **2** and **3**, **4** is diamagnetic and its NMR spectra are consistent with a $C_3$ symmetric species in solution (Figures S23−S25). Finally, IR spectroscopic studies of **4**-$^{16}$O and **4**-$^{18}$O show a feature at 815 cm$^{-1}$ in the natural abundance complex that


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shifts to 782 $cm^{-1}$ in the $^{18}O$-isotopologue as expected from a simple harmonic oscillator approximation (Figure 2B, Figure S17B). This vibrational frequency is lower than that in **3**, consistent with the slightly longer (~0.02 Å) Co−O bond length in **4**.[40,41]

The isolation of these species enabled us to investigate their reactivity with H atom donors and O atom acceptors. While **3** and **4** are thermally unstable with solution half-lives of ~6.5−8 h at room temperature (Table S2), this background reaction is sufficiently slow to allow study of their reactivity with substrates (Figure 3, Figures S26−S27). Both **3** and **4** react

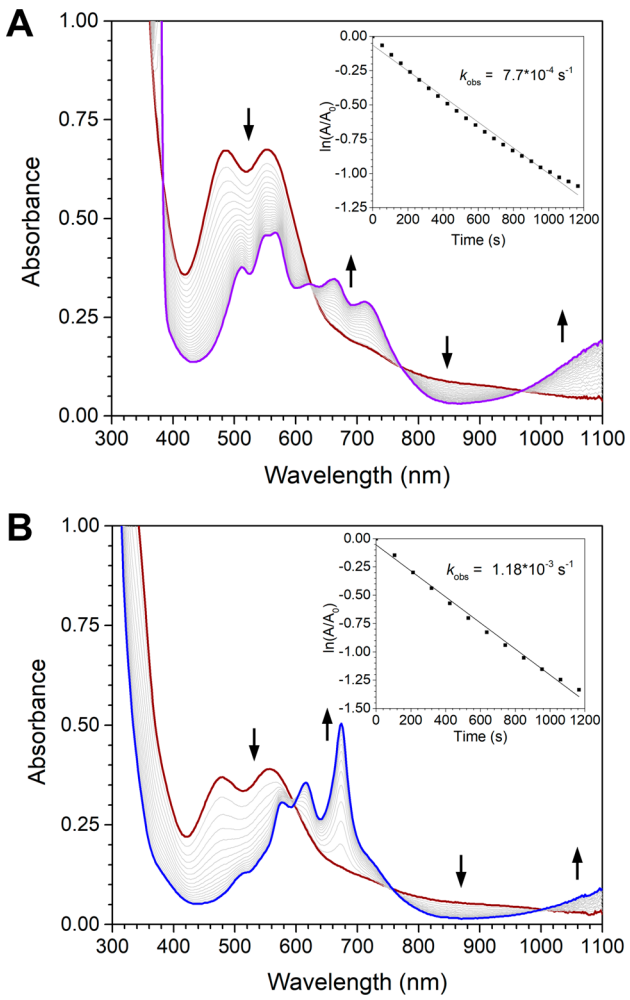


**Figure 3.** UV−vis spectra of (A) the reaction between **3** (dark red trace) and excess DHA, resulting in formation of **1** (purple trace) and (B) the reaction between **4** (dark red trace) and excess $PMe_3$ resulting in formation of $PhB(^tBuIm)_3Co^{II}Cl$ (blue trace). Gray traces indicate 1- and 2-min time intervals, respectively. Insets: first-order kinetic plots of the reaction monitored at 470 nm.

with the H atom source DHA (DHA = 9,10-dihydroanthracene) and the O atom acceptor $PMe_3$ at similar rates (Table S2). Analysis of UV−vis spectra of the reactions with DHA support the formation of anthracene and **1**, consistent with net H atom transfer. Similarly, the products of the reactions with $PMe_3$ are O═$PMe_3$ from $^{31}P$ NMR spectroscopy and what is assigned as $PhB(^tBuIm)_3Co^{II}Cl$ based on previously reported spectral data (Figures S28−S29).[35] We speculate that a putative $Co^I$ complex resulting from O atom transfer could react with adventitious chlorine atom sources such as trace dichloromethane (DCM) to give $PhB(^tBuIm)_3Co^{II}Cl$ as the major Co-containing product. Attempts to rigorously exclude DCM from the reaction solution lead to formation of O═$PMe_3$ and **1** as the major Co-containing product (Figure S30), leading us to conclude that the mechanism of this reaction is likely not a simple O atom transfer. Nevertheless, net O atom transfer from Co to P was confirmed by GC-MS analysis of the reaction mixture using $^{18}O$-labeled **3** and **4** (Figure S31).

Having established **4** as a competent H atom abstractor, we sought to estimate the bond dissociation free energy (BDFE) of the O−H bond of **1** using a thermodynamic square scheme (Scheme S1).[42] By taking the $Co^{II}/Co^{III}$ (**1**/**2**) redox potential (see above) and the p$K_a$ of the $Co^{III}$−OH (**2**), estimated at ~26 in MeCN (Figure S32), a lower bound of 85 kcal/mol for the BDFE of the O−H bond of **1** is obtained. This is consistent with not only the value of 85 kcal/mol predicted by DFT calculations (Table S3) but also the instantaneous reaction between **4** and 2,4,6-tri(*tert*-butyl)phenol (BDE ≈ 82 kcal/mol) to produce the corresponding phenoxyl radical and **1** (Figure S33).

Given their unusual nature, the bonding in **3** and **4** merits further discussion. When compared to M−E species with formal triple bonds, **3** and **4** display relatively longer M−E bonds (1.657−1.682(6) Å vs 1.50−1.59 Å) and correspondingly lower M−E stretching frequencies (800−850 $cm^{-1}$ vs 950−1000 $cm^{-1}$).[27,43,44] However, comparison to the sole example of a terminal $Co^{IV}$-oxo complex with a formal Co−O double bond shows that **3** and **4** have higher Co−O bond orders based on their bond lengths (1.657−1.682(6) Å vs 1.72 Å) and vibrational frequencies (800−850 $cm^{-1}$ vs 770 $cm^{-1}$).[15] Alternatively, comparison with isoelectronic, pseudotetrahedral $Fe^{II}$- and $Co^{III}$-imide complexes shows very similar M−O/−N bond lengths.[27] However, direct comparison of the M−E vibrational frequencies is convoluted by mixing of other ligand vibrational modes in the case of the imide complexes.[45] One notable structural difference between **4** and the related imide complexes is the off-axis tilt of the oxo ligand where the B−Co−O angle is 160.2(3)° while the B−Co−N angle in the $Co^{III}$-imide reported by Smith is 179°.[29]

To further examine the Co−O interaction in **4** we turned to density functional theory calculations (Figure 4). Analysis of the frontier orbitals reveals two Co−O $\pi^*$ interactions with $d_{xz}$ and $d_{yz}$ parentage as the two highest lying orbitals. These orbitals support the presence of two $\pi$-bonds as would be expected for a formal triple bond. The highest occupied orbital in this set is primarily of $d_{z^2}$ parentage and shows a mixed $\sigma^*$/nonbonding Co−O interaction. The lowest two orbitals are primarily of $d_{xy}$ and $d_{x^2-y^2}$ parentage and have nonbonding character with respect to the Co−O bond. This orbital picture is analogous to that in related imide complexes suggesting that the bonding in these isoelectronic species is very similar. However, the complex reported here demonstrates an off-axis tilt of the oxo ligand which is not observed in the imide complexes, although computations suggest a relatively low barrier to linearization of ~2 kcal/mol (Table S3). The preference for this bending in the oxo complex is not entirely clear but may likely be attributed to orbital mixing enabled by the weaker ligand field arising from an oxo versus an imide ligand.[46]

Taken together the results presented here unequivocally validate the assignment of a terminal $d^6$ transition metal oxo complex. The computational and experimental analyses are


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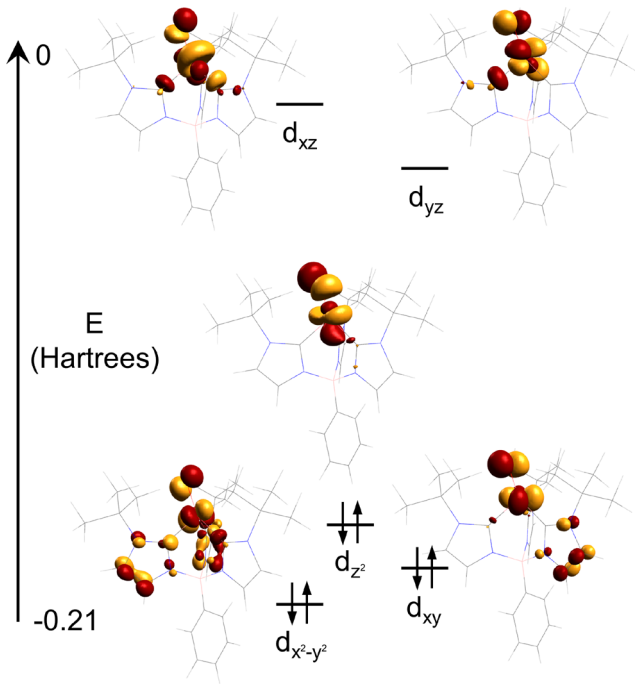


**Figure 4.** Frontier primarily Co-based molecular orbitals of **4**. The *z*-axis is oriented parallel to the energy axis shown. Note that x and y are arbitrary.

consistent with the presence of a strong Co−O interaction with multiple bond character despite a high d-electron count. While the precise nature of this bonding will be an interesting point of discussion and investigation, it is nevertheless clear that these studies provide a concrete example of this unusual class of compounds. The isolation of this complex facilitates further detailed analysis of the properties and reactivity of this and related late transition metal oxo species.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b07399.

Materials, methods, compound characterization, supplementary figures, schemes, and tables (PDF)

Crystallographic data for CoIIOH and CoIIIOH complexes and Co monomer and tetramer; xyz data for complexes **1** and **4** (ZIP)

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### Notes

The authors declare no competing financial interest.

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