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Pseudotetrahedral d^0, d^1, and d^2 Metal−Oxo Cores within a Tris(alkoxide) Platform

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Low-coordinate first-row metal complexes of d^0 [vanadium(V)], d^1 [chromium(V)], and d^2 [chromium(IV)] assume the unusual ligand field of a pseudotetrahedron when supported by a tripodal $tBu_2(Me)CO^-$ alkoxide framework. Structural, spectroscopic, and reactivity studies, supported by density functional theory calculations, indicate that the d electrons in the chromium(V) and -(IV) oxo complexes reside in metal−oxygen antibonding orbitals, engendering disparate reactivity of the metal−oxo, depending on the number of d electrons present.

Metal−oxo complexes are key intermediates for a variety of challenging transformations, among them solar fuel conversion.[1,2] The mechanism by which oxygen is delivered from a metal−oxo platform is largely determined by the coordination geometry in which the metal−oxo functionality resides.[3,4] Metal−oxo complexes of d^0−d^2-electron count in tetragonal fields feature triple bonds[5] and therefore possess an electrophilic character at the oxo that allows them to engage in acid−base chemistry with nucleophiles.[6] Alternatively, high-valent metal−oxo complexes possessing an odd d-electron count may engage in reactivity with various radical-type species. The vast majority of the well-defined metal−oxo complexes assumes a pseudooctahedral/tetragonal ligand field, and they often react as electrophiles.[7] Pseudotetrahedral metal−oxo complexes with a non-d^0-electron count are significantly less common than their pseudooctahedral/tetragonal counterparts.[8] We set out to create a well-defined coordination chemistry of pseudotetrahedral metal−oxo complexes comprising first-row transition metals and to define their structure−activity relationship.

Consideration of a reliable tripodal ligand platform for a metal−oxo in a pseudotetrahedral and oxidizing environment led us to focus on an ancillary ligand system based on sterically hindered alkoxides. In our choice of an alkoxide donor, we were motivated by the bulky alkoxide prototype tritox (tBu_3CO^-),[9,10] although the bulk of tritox, which is a perfectly symmetric cone, generally precludes coordination of three of these ligands to a metal center.[11] We surmised that the replacement of one tBu group by a Me group would transform tritox into an asymmetric cone, which would alleviate enough steric bulk to allow the formation of $M(OR)_3$ complexes. Although the $tBu_2(Me)CO^-$ (ditox) ligand can be easily prepared on a multigram scale from commercially available precursors,[12] transition-metal chemistry for this ligand has not been reported.[13] We now describe the design, structure, and reactivity of low-coordinate metal−oxo complexes in the pseudotetrahedral environment of ditox.

Figure 1 outlines the preparation of the low-coordinate M^{III} precursors and M^V−O complexes in the tris(ditox) environment. The reaction of VCl_3THF_3 with Li(ditox) leads to the formation of $[V(ditox)_3(THF)]$ (**1**), whereas for $CrCl_3THF_3$, $[Cr(ditox)_3]$ (**2**) is formed.[14] The compounds were obtained as blue (**1**) and turquoise (**2**) crystals. Complexes display trigonal-monopyramidal or trigonal-planar coordination environments, which are uncommon for an alkoxide ligand environment.[15,16] The characterization and X-ray structures of **1** and **2** are shown in the SI (Figures S1 and S2); a complete discussion of the properties of these compounds will be presented elsewhere. The pseudotetrahedral complexes, $[Cr^VX_3(O)]$ and $[Cr^{IV}X_3(O)]^-$, provide a unique opportunity to study the electronic structure of a metal−oxo possessing C_3 symmetry and a non-d^0 configuration, whereas the analogous complex, $[V^VX_3(O)]$, affords a comparison to a C_3-symmetric metal−oxo in a d^0 configuration. Oxidation of $[V^{III}(ditox)_3THF]$

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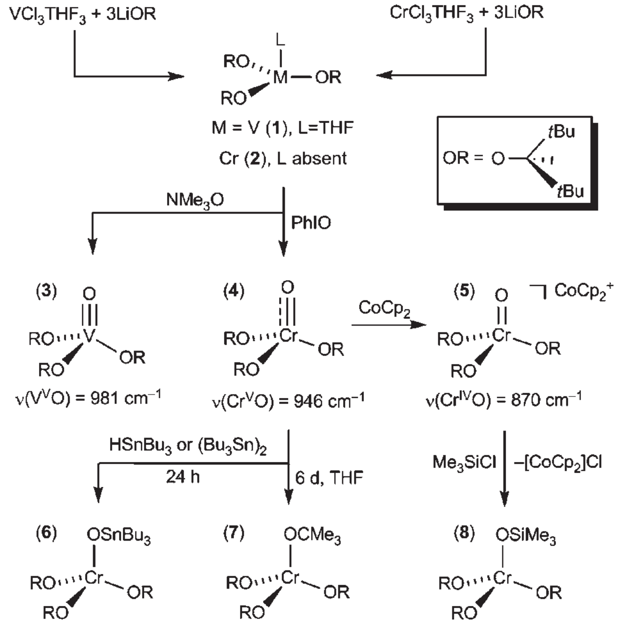

Figure 1. Synthesis and reactivity of M(ditox)$_3$O complexes.

with NMe_3O leads to [V^V(ditox)$_3$(O)] (**3**; 50% yield). Cr^V(ditox)$_3$(O) (**4**; 78% yield) was obtained via the reaction of [Cr^{III}(ditox)$_3$] with iodosobenzene. The reduction of Cr^V to Cr^{IV} was accomplished using $CoCp_2$. Light-blue crystalline [$CoCp_2$][Cr^{IV}(ditox)$_3$(O)] (**5**) was isolated in 55% yield. The NMR and electron paramagnetic resonance (EPR) data for **4** are consistent with those of a Cr^VO assignment. The ^1H NMR spectrum (C_6D_6, RT) of this d^1 metal−oxo complex displays broad and shifted resonances for tBu (1.2 ppm) and Me (3.9 ppm) groups, whereas the room temperature EPR spectrum of the chromium(V) complex (Figure S21 in the SI) shows a signal centered at $g_{iso} = 1.975$. The IR stretching frequency of the d^1 Cr−O is found at 946 cm^{-1} (Figure S9 in the SI), which is at a significantly lower frequency than those observed for typical M−O triple bonds.[17] In contrast, the V−O stretching frequency is found at 981 cm^{-1}, which is more typical for a metal−oxo triple bond. Furthermore, the IR signal for Cr−O in **5** is located at 870 cm^{-1}, which is ca. 70 cm^{-1} lower in energy than that in **4**. These observed trends for Cr−O in a pseudotetrahedral ligand field are opposite to those for Cr−O in a tetragonal field. For instance, reduction of the Cr^V center of (corrole)CrO to Cr^{IV} is accompanied by a shift of the IR stretching frequency of the Cr−O group to higher frequency,[18] as opposed to the shift of Cr−O to lower frequency in **5**.

Isomorphic crystal structures of **3** and **4** show the metal to reside in a pseudotetrahedral environment of local C_3 symmetry with the ditox ligands in an asymmetric "head-to-tail" arrangement (Figures 2 and S3 and S4 in the SI). Consistent with the IR spectra, the Cr−O bond length of 1.649(2) Å in **4** is unusually long and beyond the range of typical bond lengths of mononuclear O−Cr complexes; a CSD search spanning 25 different mononuclear Cr−O complexes displays Cr−O bond lengths in the range of 1.49−1.61 Å. Despite the slightly larger ionic radius,[19] vanadium(V) shows a shorter bond of 1.605(1) Å.

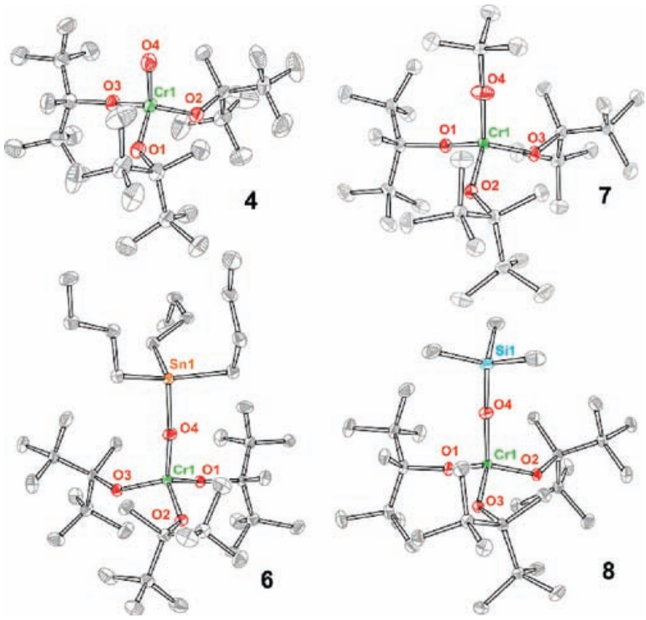

Figure 2. X-ray structures of chromium(V) and -(IV) complexes **4** and **6**−**8**. Cr1−O4 bond distances: 1.649(2) Å (**4**); 1.721(2) Å (**6**); 1.741(2) Å (**7**); 1.780(1) Å (**8**). For comparison, the V1−O4 bond distance: 1.605(1) Å (Figure S3 in the Supporting Information, SI).

The comparative spectral and structural data for vanadium(V), chromium(V), and chromium(IV) in a pseudotetrahedral coordination environment suggest that electrons populate a lowest occupied molecular orbital possessing significant π^* M−O character. To assess this contention, the reactivity of Cr^V−O and Cr^{IV}−O has been explored. Because the presence of a single electron at the π^* M−O molecular orbital may lead to a radical character at the oxo, **4** was treated with compounds that possess X−Y bonds prone to homolytic cleavage. Compound **4** reacts with $HSnBu_3$ to furnish the green chromium(IV) product **6** (33% yield of pure isolated product). The crystal structure of **6** (Figure 2) verifies a chromium(IV) formulation in which the oxo ligand is transformed into a stannoxo group. As a possible scenario for the reaction mechanism, we invoke the initial formation of Cr^{IV}−OH, along with Cr−$OSnBu_3$ (Figures S22 and S23 in the SI). While the Cr^{III}−OH moiety is viable,[20] Cr^{IV}−OH is expected to be very acidic,[21] eventually leading to ditox hydrolysis. Significant amounts of the free ligand formed during the course of the reaction (ditoxH) provide indirect evidence for the formation of Cr^{IV}−OH (the sample was kept under rigorously dry conditions). The reaction of **4** with $Bu_3SnSnBu_3$ leads to the same compound in higher isolated yield (55%). It should be noted that while diamagnetic and highly oxidizing chromium(IV) compounds are known to abstract hydrogen atoms while not possessing radical character,[22] chromium(V) is significantly less oxidizing (−0.74 V for the Cr^V/Cr^{IV} couple vs $FeCp_2^+/FeCp_2$; Figure S24 in the SI).

Compound **4** undergoes slow decomposition at room temperature over the course of several days to yield a C−O

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bond at the oxo (**7**; Figure 2) with or without additional reagents (2,3-dimethylbutadiene, *tert*-butyl peroxide, TEMPO, etc.) present. Compound **7** is isolated in pure form by crystallization from pentane (ca. 30% isolated yield); the compound was characterized by X-ray crystallography, IR spectroscopy, and elemental analysis. With the exception of the absence of 946 cm^{-1} Cr–O absorption (Figure S18 in the SI), its IR spectrum is virtually identical with that of **4**. A possible route to the formation of **7** likely involves the reaction of a tBu radical, originating in the ditox ligand, with an oxo.

Square-pyramidal chromium(V) oxo complexes, featuring an M–O triple bond, display reactivity indicative of an electrophilic oxo group.[5,6] Compound **4** oxidizes PPh_3. The reaction of **4** with 1 equiv of PPh_3 for 12 h leads to a mixture of PPh_3 and PPh_3O, in addition to a green unidentified metal-containing product (Figure S25 in the SI). In contrast, **4** does not show any reactivity at the oxo toward BPh_3. Compound **4** oxidizes Ph_2PPPh_2 to give $Ph_2P(O)PPh_2$ quantitatively within a few hours (Figure S26 in the SI), whereas **5** shows no oxo transfer to diphosphine within 24 h (Figure S27 in the SI). Further insight into the reactivity of the M–O group in chromium(V) and -(IV) complexes was furnished using Me_3SiCl as the reactant. While the chromium(V) oxo complex does not react with Me_3SiCl in the course of 4 h, the reaction of chromium(IV) oxo with Me_3SiCl is instantaneous. $[Cr(ditox)_3(OSiMe_3)]$ (**8**) is isolated in 77% yield as green crystals; the compound has been characterized by IR spectroscopy, elemental analysis, and X-ray crystallography (Figure 2). The above reactivity is consistent with the oxo group being electrophilic in **4** and nucleophilic (double bond) in **5**.

Density functional theory calculations were performed to aid in the interpretation of spectral, structural, and reactivity data. The tBu groups of **4** and **5** were replaced by Me groups in order to simplify the calculations. The calculated Cr–O bond distances obtained from the geometry optimizations of the models, **4′** and **5′**, were 1.59 and 1.61 Å, respectively; these bond lengths are in agreement with the geometric parameters observed in the crystal structures of **4** and **5** (for the structure of **5**, see Figure S5 in the SI). Moreover, a trend consistent with the experimental results in the calculated Cr–O vibrational stretching frequencies for **4′** (1039 cm^{-1}) and **5′** (988 cm^{-1}) is observed.

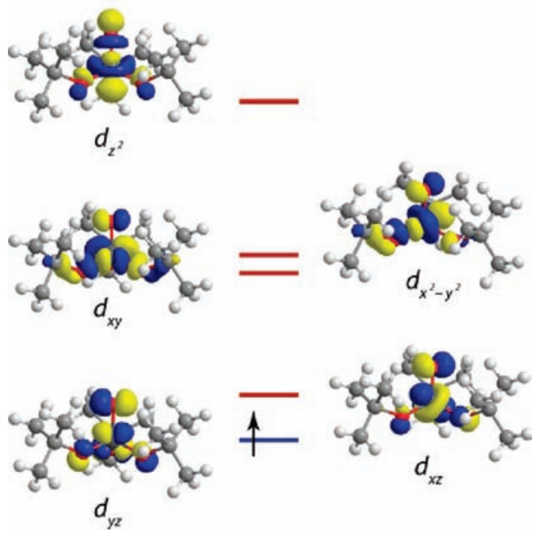

Figure 3. Pictorial representation of the frontier molecular orbitals for the model of **4** plotted at the 0.04 isodensity.

The frontier orbitals of **4′** (Figure 3) provide insight into the electronic structure and reactivity of **4**. The highest singly occupied molecular orbital (SOMO) corresponds to the d_{yz} Cr orbital, whereas the lowest unoccupied molecular orbital (LUMO) shows the d_{xz} orbital to participate in an antibonding π^* interaction with the apical O p orbitals. The significant O orbital character, ~16% in the SOMO, is consistent with the radical behavior of **4**. The LUMO+1 corresponds to the pseudodegenerate (d_{xy}, $d_{x^2-y^2}$) orbital set, which displays significantly less O p orbital character (6%). Conversely, the alkoxide orbitals participate in a sizable (~24%) σ^*-antibonding interaction, which results in significant destabilization of the d_{xy} and $d_{x^2-y^2}$ orbitals. This electronic interaction is intrinsic to the ancillary set of strong π (alkoxide) donors. The net result of this interaction is that the d_{yz} and d_{xz} orbitals lower the energy of the d_{xy} and $d_{x^2-y^2}$ orbitals. The electronic structure of **5** follows a similar molecular orbital scheme, where the two highest singly occupied orbitals are d_{yz} and d_{xz}. The triplet multiplicity was confirmed by SQUID magnetometry (Figure S31 in the SI).

In summary, we have prepared pseudotetrahedral d^1 Cr^V and d^2 Cr^{IV} metal–oxo complexes in the oxygen-rich environment of terminal alkoxides. In both species, d electrons reside in the Cr–O antibonding orbitals to engender a Cr–O bond order of less than 3. Evaluation of the reactivity of the d^1 (reacts with electrophiles and radicals) and d^2 (nucleophilic) metal–oxo complexes **4** and **5** is consistent with this unusual electronic structure of a metal–oxo. Elaboration of additional metal–oxo complexes of this tris(alkoxide) system is currently underway.

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Supporting Information Available: X-ray crystallographic data in CIF format, experimental procedures, synthesis and characterization of compounds, IR and EPR spectra, X-ray crystallographic details, computational details, and Cartesian coordinates of models of **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.