Dinuclear Complexes

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Dioxygen Activation by Siloxide Complexes of Chromium(II) and Chromium(IV)[**]

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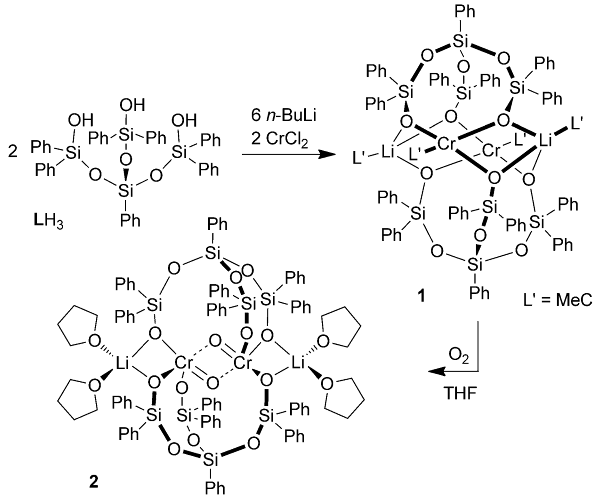
***Abstract:** The reaction of a tripodal trisilanol with n-butyllithium and $CrCl_2$ results in a dinuclear Cr^{II} complex (**1**), which is capable of cleaving O_2 to yield in a unique complex (**2**) with an asymmetric diamond core composed of two Cr^{IV}=O units. Magnetic susceptibility data reveal significant exchange coupling of Cr^{II} ($S=2$) in **1** and large zero-field splitting for Cr^{IV} ($S=1$) in **2** owing to strong spin–orbit coupling of the ground state. The Cr^{IV}=O compound can also be generated using PhIO, and evidence was gathered that although it is the stable product isolated after excessive O_2 treatment, it further activates O_2 to yield an intermediate species that oxidizes THF or Me-THF. By extensive ^{18}O labeling studies we were able to show, that in the course of this process $^{18}O_2$ exchanges its label with siloxide O atoms of the ligand via terminal oxido ligands.*

The utilization of bulk hydrocarbons as feedstocks for commodity and fine chemicals typically requires an oxidation step that usually has to be mediated by a metal compound, as cheap and green oxidants such as O_2 are too unreactive without a prior activation. Chromium(II) compounds have been shown to be capable of dioxygen activation. Early work brought evidence for this spectroscopically,[1,2] and in the late 1990s the first chromium(IV) oxo complexes were structurally characterized.[3,4] Within the last years it has been shown, in particular by Nam and Theopold, that molecular chromium(II) centers, ligated by nitrogen donors, in contact with dioxygen formed reactive species featuring superoxido, peroxido, and oxido ligands.[5–9] We believed that siloxide surroundings could lead to novel reactivity in this regard, as chromium(II) sites embedded in a silica matrix are known to have rather special electronic properties, that therefore guarantee the activity of the Phillips catalyst[10,11] employed for the industrial polymerization of ethylene. Indeed, herein we describe O_2 cleavage at a molecular Cr^{II} siloxide to yield a complex with an unprecedented dinuclear $(Cr^{IV}{=}O)_2$ core, and importantly, dissolved in THF this further activates O_2 for THF oxidation, a process that is accompanied with unique incorporation of ^{18}O label into the siloxide ligand.

Recently we described a new tripodal trisilanol (LH_3; Scheme 1)[12] which was deprotonated in THF with three equivalents of n-butyllithium. After addition of one equivalent of $CrCl_2$, workup, and recrystallization from acetonitrile/diethylether provided blue, block-shaped crystals, and an X-ray diffraction analysis (Figure 1) revealed that the reaction had led to a dinuclear chromium(II) complex $[L_2Cr_2(MeCN)_2][\{Li(MeCN)\}_2]$ (**1**).



Scheme 1. Synthesis of complexes **1** and **2**.

The tripodal ligands coordinate with two of their arms to one chromium(II) center, each thereby forming two eight-membered siloxide–chromium rings, whereas the other arms coordinate to the adjacent chromium(II) centers. Both chromium atoms complete their almost perfectly square-planar coordination sphere by an acetonitrile ligand. Inversion symmetry affords that the two Cr^{II} coordination planes, being connected by two Li ions, are co-planar with a Cr–Cr distance of 3.2606(10) Å. The Cr–O bond lengths range from 1.9978(11)–2.0642(11) Å with *trans* O-Cr-O angles of 178.37(5)° and *cis* angles of 85.66(4)° for O1-Cr1-O5′ and 93.44(5) for O5′-Cr1-O6, respectively. The two lithium ions bind to three of the siloxide donor functions as well as to one additional acetonitrile molecule each. The bond parameters compare well with those of other mononuclear[13] and dinuclear[14,15] chromium(II) siloxide complexes. For these and other Cr^{II} complexes, square-planar ligand geometries

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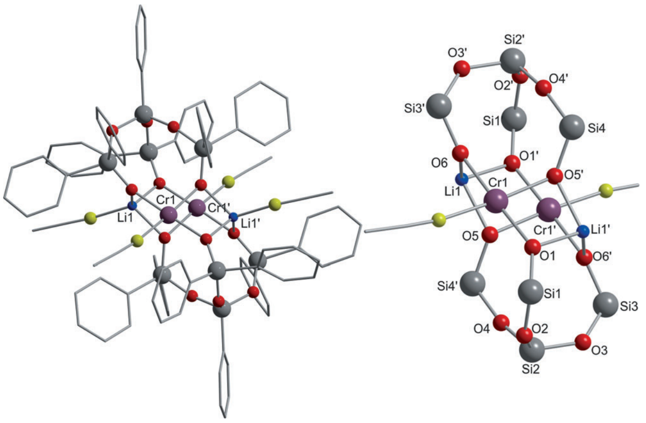


Figure 1. Molecular structure of **1** (left) and its core motif (right).[32] Structural parameters are given in the Supporting Information, Figure S5.

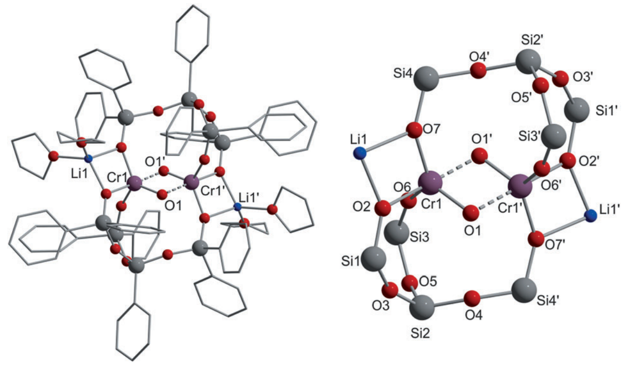


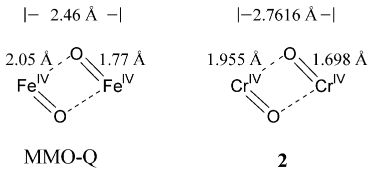
Figure 2. Molecular structure of **2**·2 toluene (left) and its core motif (right).[32] Structural parameters are given in the Supporting Information, Figure S6.

were often found, but only for a few representatives the magnetic and electronic properties have been investigated.[16–18] In case of complex **1**, we measured an effective magnetic moment of 6.1 μ_B at room temperature, which is slightly less than the spin-only value of 6.9 μ_B expected for two uncoupled chromium(II) ions with spin $S=2$. The effective moment decreases smoothly with temperature to reach 0.8 μ_B at 2 K (Supporting Information, Figure S8). The behavior can be perfectly simulated with weak exchange coupling of the two spins with $J=-10.6(\pm 1)\ \mathrm{cm}^{-1}$ (notation $H=-2JS_1S_2$, with 5% impurity of chromium(III)), but not with zero-field splitting of the $\mathrm{Cr^{II}}$ ions only. Therefore, a remarkably strong long-distance coupling of the separate chromium(II) ions is present in **1**, mediated by the relatively long chains of bridging oxygen and lithium ions. Very similar behavior of $\mu_{\mathrm{eff}}(T)$ was previously observed for the sodium congener of a classical lithium methylchromate dimer,[16] which also has two planar chromium(II) moieties, bridged by sodium ions in that case. Although the explicit coupling constant was not determined, the mean-field Weiss constant $\Theta=-71$ K (see the Supporting Information of the report) indicates in fact also strong exchange coupling. Even stronger interaction with $\Theta=-115$ K was reported for a dimeric chromium(II) aryloxide complex with an isostructural core of sodium-bridged $\mathrm{Cr^{II}O_4}$ planes.[18] We therefore suggest that direct overlap of the magnetic d_{z^2} orbitals in such facially oriented chromium(II) coordination planes contributes substantially to the antiferromagnetic coupling of the metal ions, indicating onset of weak metal–metal bonds.

When **1** was dissolved in THF and treated at room temperature with an excess of O_2, the solution immediately changed color from rose to brownish-yellow, and after recrystallization of the crude material from toluene/*n*-hexane, reddish brown, block-shaped crystals could be isolated, the X-ray crystal structure analysis of which revealed that **1** had cleaved O_2 to yield a dinuclear chromium(IV)oxo complex $[L_2Cr_2O_2][Li(THF)_2]_2$ (**2**) with an unusual asymmetric Cr_2O_2 diamond core (Figure 2). The Cr1−O1/Cr1′−O1′ distances of 1.698(3) Å are in the range of bond lengths reported for $\mathrm{Cr^{IV}{=}O}$ double bonds.[8,19,20] In contrast, the Cr1⋯O1′/Cr1′⋯O1 distances of 1.955(3) Å are considerably longer and thus argue against a bis-μ-oxido core, the structural motif that previously has been observed[3,4] to form after O_2 activation at $\mathrm{Cr^{II}}$ complexes (apart from mononuclear complexes[4–8]). DFT calculations (see the Supporting Information) reproduced the solid-state structure and thus confirmed that the asymmetry is not circumstantial but has electronic reasons. We are not aware of comparable molecular complexes with two M=O units arranged in a diamond core. Structural characterization of such is of relevance also for biological systems:[21] The key intermediate formed in course of O_2 activation by the soluble methane monooxygenase (MMO-Q) is, according to detailed spectroscopic data, best described as a strongly coupled diiron(IV) species with a Fe⋯Fe separation of 2.46 Å and two unequal Fe−O bonds of 1.77 and 2.05 Å, respectively.[22]

Although it is based on a different metal, complex **2** thus shows striking similarities to MMO-Q (Scheme 2): Both are generated by setting out from a dinuclear metal(II) state, and O_2 activation leads to an asymmetric diamond core with the metals in the oxidation states +IV and very similar interatomic distances.

To further elucidate the electronic structure and metal coupling of the unusual Cr_2O_2 core of **2**, we measured its magnetic properties. Above about 150 K, complex **2** as a solid shows a temperature-independent effective magnetic moment of 4.2 μ_B (Supporting Information, Figure S11A). As the value is very close to the spin-only value of 4 μ_B for two uncoupled spins $S=1$, the diamond core of **2** can have only weak exchange interaction, $J \ll kT$. Below 150 K $\mu_{\mathrm{eff}}(T)$ drops



Scheme 2. Comparison of structural parameters of the active site of the key oxidizing intermediate of sMMO (MMO-Q) and the core motif of **2**.

monotonously and reaches about 3 μ_B at 2 K, whereas multi-field data sampled at 1, 4, and 7 T (Supporting Information, Figure S11B) show only moderate nesting of magnetization $M(\mu_B B/kT)$. Both features reveal large zero-field splitting of chromium(IV), meaning that only a few magnetic substates are low-lying in energy (Supporting Information, Figure S12). A corresponding spin Hamiltonian simulation yields an excellent global fit to both sets of magnetic data with weak positive spin coupling, $J = 2.0(\pm 1)\ \mathrm{cm^{-1}}$, and large zero-field splitting with $D = -53(\pm 8)\ \mathrm{cm^{-1}}$ ($E/D = 0.04 \pm 0.04$). For an initial explanation, we suggest that the ligand field of the chromyl units is dominated by the short chromium(IV) oxo bonds so that the two sites may be regarded approximately as pseudo-linear or distorted square-pyramidal complexes (note that chromium(V) nitrido complexes show pseudo-linear ligand-field splitting, irrespective of the nature of the supporting coordination framework[23]). If then strong π interaction with oxygen leads to splitting of the low-lying t_{2g} orbitals in d_{xy} and quasi-degenerate first excited $\{d_{xz}/p_x\}$, $\{d_{yz}/p_y\}$ orbitals, spin–orbit coupling within the nearly-degenerate orbital ground state of the resulting $(d_{xy})^1(\{d_{xz}/p_x\}/\{d_{yz}/p_y\})^1$ configuration would explain the strong zero-field splitting of $\mathrm{Cr^{IV}{=}O}$. But also the weak spin coupling in the dinuclear core is plausible, because neither the magnetic d_{xy} and d'_{xy} orbitals of Cr1 and Cr1′ nor the magnetic MOs $\{d_{xz}/p_x\}$ and $\{d_{yz}/p_y\}$ of Cr1=O1 and Cr1′=O1′ moieties should have significant overlap owing to the misdirected orientation of the Cr=O units in the diamond core (Supporting Information, Scheme S2). Electrostatic interaction between the half-filled t_{2g} orbitals of the two sites in this case should yield in fact (weak) ferromagnetic spin coupling;[24] according to the classical Goodenough–Kanamori rules, this holds also for residual overlap between half-filled and empty orbitals.[25,26] Weak ferromagnetic interaction is thus not unexpected for two chromium(IV) oxo sites with $3d^2$ configuration arranged in such a diamond core.

Complex **2** is stable for days in solution as well as in the solid state at room temperature, but the ESI-MS(−) of a THF solution not only showed the signal for its monomeric version $[\mathrm{LCr^{IV}O}]^-$ at $m/z = 815.09$ but also signals for species with higher O content (see the Supporting Information), which might be due to disproportion of **2** under ESI conditions. As **1** (or its monomeric version) is highly sensitive towards O_2, it could not even be detected in ESI-MS studies: Owing to the presence of O_2 in the mass spectrometer, solutions of **1** in THF only led to peaks indicating oxygenation, with the most prominent peak at $m/z = 815.09$ corresponding to monomeric **2**, which is denoted **2′** (Figure 3). All attempts to exclude O_2 in the mass spectrometer and thus to detect **1** by mass spectrometry failed. Treatment of a THF solution of **1** with two equivalents of PhIO instead of O_2 also led to the formation of **2**, as shown by UV/Vis spectroscopy and ESI-MS (see the Supporting Information), while N_2O did not react. By contrast, Copéret et al. recently reported a dinuclear chromium(II) siloxide, $[\{\mathrm{Cr(OSi(O}t\mathrm{Bu)_3)_2}\}_2]$, which did react with N_2O; however, to a corresponding chromium(III) complex lacking terminal oxido ligands.[15] This illustrates well the subtle influence the siloxide environment has on the $\mathrm{Cr^{II}}$ reactivity.

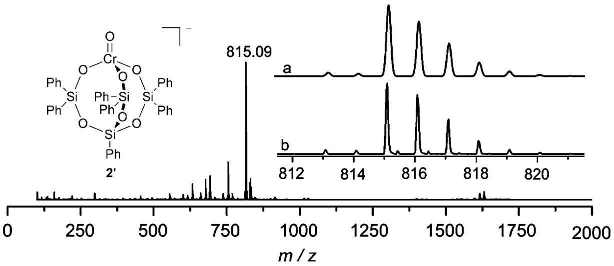


Figure 3. ESI-MS(−) of a THF solution of **1** with a signal for $[\mathrm{LCr^{IV}O}]^-$ (**2′**) and its putative structure (inset). a) The calculated signal for **2′** and b) the relevant section of the spectrum of **2′**.

An unexpected observation was made in an ESI-MS analysis, after $^{18}O_2$ had been used for the oxidation of **1** in THF, which in this context proved unique as a solvent (see below): Instead of a simple shift of all peaks belonging to $[\mathrm{LCr^{IV}O}]^-$ by $m/z = 2$ a complex signal was obtained that indicated incorporation of more than one ^{18}O atom (Figure 4).

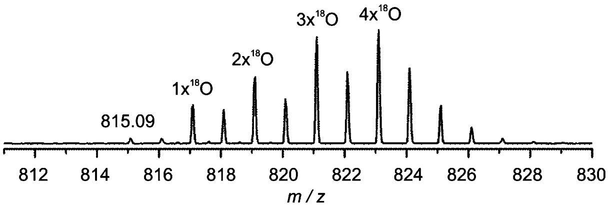


Figure 4. Section of the ESI-MS(−) spectrum of a THF solution of **2** prepared by $^{18}O_2$ treatment of **1** showing the m/z range for **2′**.

This suggested that not only the Cr=O functionality was isotopically labeled: $^{18}O/^{16}O$ exchange also occurred for O atoms belonging to L^{3-}. To confirm this, the reaction mixture of $[^{18}O]$-**2** prepared this way was subsequently hydrolyzed with a diluted HCl solution to cleave the metal siloxide bonds in complex **2** by protonation of the $\mathrm{Si{-}O^-}$ functions, and without further workup the solution was analyzed by mass spectrometry. The ESI-MS(+) spectrum showed a prominent peak at $m/z = 773.16$ assigned to $[\mathrm{LH_3Na}]^+$ and again additional peaks that are shifted by $m/z = 2$, 4, and 6 were observed (Figure 5). From these experiments it is evident that in course of the oxidation of **1** by $^{18}O_2$ ^{18}O atoms are also incorporated into L^{3-}, and isotopologues that bear up to four ^{18}O atoms for $[\mathrm{LCr^{IV}O}]^-$ and up to three ^{18}O atoms in case of $[\mathrm{LH_3Na}]^+$, respectively, result; a very similar incorporation of ^{18}O was observed when using an excess of $\mathrm{PhI^{18}O}$ as the oxidant for a THF solution of **1**. Incorporation of the ^{18}O into L^{3-} might be explained by a shift of the silyl groups to intermediate terminal oxido ligands; to our knowledge this type of reactivity has been observed neither for alkoxide nor siloxide complexes so far. There is only precedence for Claisen-like rearrangements in case of allylic residues[27] (whose C=C units are thus involved) and slow oxido–hydroxido tautomerization.[28]

Even more remarkably, it turned out that upon treatment of THF solutions of **2** either with $^{18}O_2$ or an excess of $\mathrm{PhI^{18}O}$ again the incorporation of several ^{18}O atoms into **2** occurred,

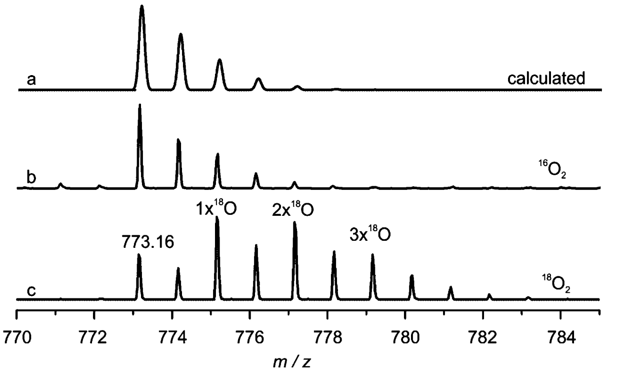
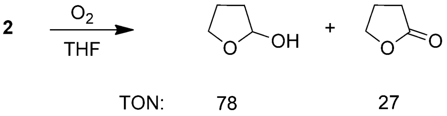


Figure 5. Sections of ESI-MS(+) spectra showing the *m/z* range for $[LH_3Na]^+$. a) calculated spectrum for $[LH_3Na]^+$; b) the signal for $[LH_3Na]^+$ after treating **1** in THF with $^{16}O_2$ followed by hydrolysis; c) the signal for $[LH_3Na]^+$ after treating **1** in THF with $^{18}O_2$ followed by hydrolysis.

as a signal similar to the one displayed in Figure 4 was observed (see the Supporting Information). On the other hand it was found that $H_2{}^{18}O$ exchanges its label under O_2-free conditions exclusively with the terminal oxido ligands in **2** or its monomer **2′**, respectively: In an ESI-MS(−) analysis after $H_2{}^{18}O$ treatment the signal of $[^{16}O]$-**2′** appeared shifted by two mass units (see the Supporting Information). However, when O_2 was added to **1** or **2** in the presence of $H_2{}^{18}O$, scrambling of O atoms belonging to the ligand occurred. Taken together, these findings clearly indicate that **2**, although it is stable and the apparent end product of the O_2 oxidation of **1**, does in fact react with O_2 and PhIO.

We then set out to explore the fate of the oxygen after activation by **2**. One conceivable explanation was the reversible formation of an intermediate "O_2 complex", which exchanges the label between $^{18}O_2$ and the terminal $Cr^{IV}{=}O$ functions as well as with the adjacent siloxide functions. However by gas-phase mass spectrometry we could exclude the presence of $^{16}O^{18}O$ in the gas phase after exposure of **1** or **2** to $^{18}O_2$. Another observation was that a large excess of PhIO (ca. 15 equiv, an amount that is usually insoluble in common organic solvents) was fully dissolved within hours in contact with THF solutions either of **1** or **2**. However, analyzing the gas phase after such experiments by GC no O_2 could be detected. Compound **2** thus reacts with oxidants, accepting O atoms, but subsequently no O_2 is released. After treatment of **1** dissolved in THF with O_2 (in darkness), analysis by GC-MS and ^{1}H NMR spectroscopy indicated the presence of oxidation products originating from THF in the reaction mixture, as, for instance, 2-hydroxytetrahydrofurane and γ-butyrolactone, which are common oxidation products of THF (Scheme 3).[29] These products were also detected by GC-MS from the crude reaction mixture, when PhIO was employed as the oxidant.Additionally, minor amounts of unidentified products were present in the crude reaction mixture. The turnover numbers, calculated per chromium atom, are comparable to those reported previously for Fe^{III} silsesquioxane compounds[30] and reveal **2** as a potent catalyst for THF oxidation. As **2** itself does not react with THF in the absence of O_2, the product resulting from O_2 activation at **2** must be responsible for THF oxidation. We exclude uncatalyzed reaction between THF and O_2 for the following reasons: 1) THF oxidation also occurs employing PhIO as the oxidant (see above); and 2) no oxidation occurred in the absence of **2**.[31]



Scheme 3. Identified products of the oxidation of THF by **2** in the presence of dioxygen and their corresponding turnover numbers (TON). Quantification of the formed products was performed by ^{1}H NMR of the crude reaction mixture using TMS as an internal standard (Supporting Information, Figure S1).

To shed more light on the scrambling mechanism of **2** and the oxidation of THF, we systematically analyzed the oxidation of **1** by $^{18}O_2$ in further solvents. While for 2-methyl-THF the same observations as in the case of THF could be made (γ-methyl-γ-butyrolactone could be detected by GC-MS from the crude reaction mixture), NMR spectroscopic investigations provided no hints to solvent oxidation when the reactions were carried out in dichloromethane, benzene, toluene, or 1,4-dioxane. Interestingly, in parallel in none of these solvents an incorporation of ^{18}O into L^{3-} could be observed, so that apparently this kind of scrambling is coupled to substrate oxidation. Therefore, either the active species is not capable of oxidizing these solvents or it is not formed in them. We assume the latter, as in these solvents the addition of sacrificial and easily oxidizable substrates, such as triphenylphosphine, 1,4-cyclohexadiene, benzaldehyde, 1-benzyl-1,4-dihydronicotinamide did not lead to oxidation/scrambling.

We explain these observations as follows: **1** reacts with O_2 to give **2** or its monomer **2′** in solution. In contact with O_2 a species is formed, which is capable of oxygenating THF catalytically. During this process it exchanges its oxido ligands with O atoms belonging to the ligand, so that O atoms derived from O_2 are incorporated into the ligand framework, and the experiment with $H_2{}^{18}O$ shows that terminal Cr=O units are involved. As those of **2** do not exchange with the ligand O atoms in the absence of O_2, they must belong to the oxidized species.

In summary, we report herein a novel dinuclear chromium(II) siloxide complex capable of cleaving O_2 to yield a unique complex with an asymmetric diamond core composed of two $Cr^{IV}{=}O$ units. Furthermore, we obtained evidence that also the $Cr^{IV}{=}O$ compound can further activate O_2 to yield an intermediate species that oxidizes THF, and by extensive ^{18}O labeling studies we were able to show that in the course of this process $^{18}O_2$ exchanges its labels with siloxide O atoms of the ligand. In future work we will now elucidate the unique role of THF in supporting the active species and determine the scope of oxidations that can be performed by this system.

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Keywords: chromium · dioxygen activation · oxido complexes · scrambling · siloxides

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[31] Employing $CrCl_2$ or $[Cr_2(OAc)_4(H_2O)_2]$ instead of **2** in an analogous procedure THF oxidation could also be observed but with significantly lower TONs, and the ratios between alcohol and lactone were not 3:1 as in case of **2** but close to 1.
[32] CCDC 996284 (**1**) and CCDC 996285 (**2**·2 toluene) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.