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The Direct Oxidative Addition of O_2 to a Mononuclear Cr(I) Complex Is Spin Forbidden

Fang Dai, Glenn P. A. Yap, and Klaus H. Theopold*

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

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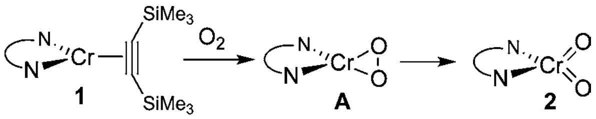
ABSTRACT: Mononuclear chromium(I) alkyne complex $(i\text{-Pr}_2\text{Ph})_2\text{nacnacCr}(\eta^2\text{-C}_2(\text{SiMe}_3)_2)$ (**1**) reacts rapidly with dioxygen to yield chromium(V) dioxo species $(i\text{-Pr}_2\text{Ph})_2\text{nacnacCr(O)}_2$ (**2**). The mechanism of this oxygen cleavage has been studied experimentally and computationally. Isotope labeling studies rule out a direct four-electron oxidative addition of O_2 to one chromium atom, which involves a spin-forbidden transformation. Instead, the reaction likely proceeds via an unsymmetric binuclear chromium bis(μ-oxo) complex. The latter has been independently prepared and structurally characterized. Its reactivity with O_2 is consistent with the proposed mechanism.

The metal-mediated cleavage of the O−O bond of dioxygen and its microscopic reverse (preceding O_2 evolution) are chemical transformations of considerable importance, due to their central role in aerobic oxidation catalysis[1] and energy storage via the splitting of water,[2] respectively. While this elementary reaction could in principle occur in the coordination sphere of a single metal atom, we are in fact not aware of any system where this has been unambiguously shown to be the case,[3] and it has even been suggested that this transformation can be symmetry forbidden.[4] It is thus of interest to establish whether a single metal atom is sufficient to make or break the O−O bond of O_2. Accordingly, when our exploration of the reactivity of chromium compounds in the formal oxidation state +I presented us with an apparent example of a facile four-electron oxidative addition of O_2 to a single metal, we chose to investigate the mechanism of this reaction. Herein we report that the reaction is indeed more complicated than it seems at first sight.

We have previously described the reaction of Cr(I) synthon $[(i\text{-Pr}_2\text{Ph})_2\text{nacnacCr}]_2(\mu\text{-N}_2)$ with O_2, which yielded brown Cr(V) dioxo complex $(i\text{-Pr}_2\text{Ph})_2\text{nacnacCr(O)}_2$ (**2**).[5] While the dinitrogen complex obviously fulfills one of the necessary conditions, namely the availability of four (or more) electrons per metal atom for the complete reduction of O_2, its dinuclear nature obscures the conceptual simplicity of the reaction we wish to study. Therefore we have prepared a closely related mononuclear reactant; KC_8 reduction in THF of $[(i\text{-Pr}_2\text{Ph})_2\text{nacnacCr}(\mu\text{-Cl})]_2$ in the presence of bis(trimethylsilyl)acetylene produced the mononuclear alkyne complex $(i\text{-Pr}_2\text{Ph})_2\text{nacnacCr}(\eta^2\text{-C}_2(\text{SiMe}_3)_2)$ (**1**) in 60% isolated yield. Dark-green **1** is paramagnetic ($\mu_{\text{eff}}(\text{RT}) = 3.9(1)\ \mu_B$), and its molecular structure (determined by X-ray diffraction) showed it to be an analog of recently described $(i\text{-Pr}_2\text{Ph})_2\text{nacnacCr}(\eta^2\text{-C}_2(\text{Ph})_2)$.[6] While the structural features of **1** support a description as a Cr(III) metallacyclopropene, steric repulsion between its bulky substituents renders it substitutionally labile. In its reactions, **1** releases the alkyne, and thus it commands the full d^5 complement of electrons of a Cr(I) compound.

The reaction of **1** in THF with O_2 is immediate, even at low temperature, resulting in a color change from green to brown without any visible intermediate stages. In a similar vein, monitoring the reaction at −78 °C by in situ IR spectroscopy did not reveal any reaction intermediates. ^{1}H NMR spectroscopy showed **2** and free bis(trimethylsilyl)acetylene as the sole products, and the Cr(V) dioxo complex **2** could be crystallized from the mixture in 60% yield. Stopped-flow kinetic measurements carried out at low temperature showed the reaction to be first order in both [**1**] and [O_2], with a second-order rate constant of $k_2(213\text{ K}) = 440\ \text{M}^{-1}\ \text{s}^{-1}$, i.e., a rather fast reaction. The simplest interpretation of these observations involves a rate-limiting ligand substitution of O_2 for alkyne, followed by a rapid oxidative addition of the O_2-ligand of the resulting dioxygen complex **A**, cleaving the O−O bond and thus forming the observed product (see eq 1).

(1)



This proposed mechanism makes a straightforward prediction regarding the outcome of an isotope labeling experiment. Absent rapid intermolecular scrambling of O-atoms in **2**, a reaction with an equimolar mixture of $^{16}O_2$ and $^{18}O_2$ should yield only $\mathbf{2}(^{16}\text{O})_2$ and $\mathbf{2}(^{18}\text{O})_2$. A control experiment established that the scrambling of oxygen atoms between independently prepared $\mathbf{2}(^{16}\text{O})_2$ and $\mathbf{2}(^{18}\text{O})_2$ is indeed relatively slow; after 30 min at ambient temperature, an equimolar solution of the former in THF contains only 15% of the mixed isotopolog, i.e., $\mathbf{2}(^{18}\text{O})(^{16}\text{O})$. However, exposure of a THF solution of **1** to a $^{16}O_2/^{18}O_2$ mixture (1:1), followed by analysis, by LIFDI-MS[7], 15 min after mixing, produced the three possible isotopologs of **2** in the statistical ratio of 1:2:1. This result *rules out* the direct binding and subsequent oxidative addition of O_2 to the chromium atom of **1** in an intramolecular process.

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A well precedented pathway for O−O bond cleavage consists of binding of a second metal to the initially formed dioxygen complex (e.g., **A**), followed by rearrangement to a bis(μ-oxo) species,[8] which may then react further with dioxygen. To gauge the possibility of such a pathway, we attempted to prepare such a dinuclear intermediate. Reaction of **1** with half an equivalent of oxygen formed a new dichromium complex, namely [(*i*-$Pr_2Ph)_2$nacnacCr]$_2$(μ-O)$_2$ (**3**). **3** could also be prepared by mixing equimolar amounts of **1** and **2**. The result of an X-ray crystal structure determination of **3** is shown in Figure 1. It exhibits a positional disorder of the oxygen atoms, which has been modeled as part of the refinement (see SI).

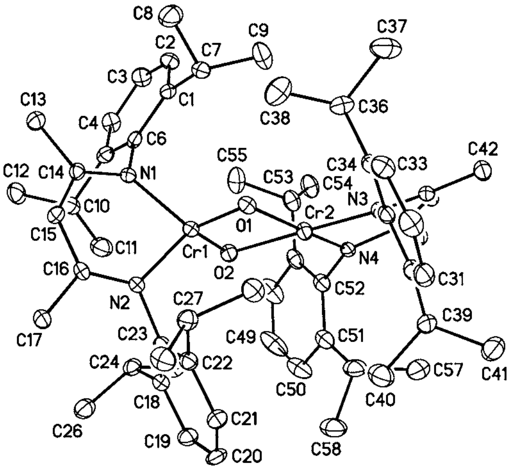


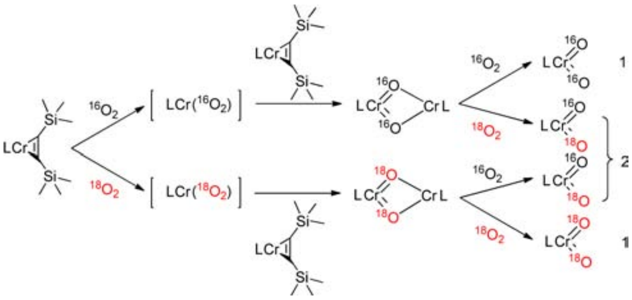
Figure 1. Molecular structure of **3** (30% probability level); Selected interatomic distances (Å) and angles (°): Cr1−O1, 1.682(3); Cr1−O2, 1.683(3); Cr2−O1, 2.018(3); Cr2−O2, 2.034(3); O1−Cr1−O2, 98.69(15); O1−Cr2−O2, 78.11(12). Only the major (84%) of two disordered, but equivalent, structures is shown.

3 features an unusual asymmetrical structure. The bridging oxygen atoms have significantly shorter bonds to Cr1 (Cr1−O: 1.682(3), 1.683(3) Å) than to Cr2 (Cr2−O: 2.018(3), 2.034(3) Å). In addition, the coordination geometry of Cr1 is pseudotetrahedral, while that of Cr2 is square planar. We suggest that **3** is a mixed-valent complex, best formulated as containing Cr(IV) and Cr(II), based on structural parameters. **3** is paramagnetic; its room-temperature effective magnetic moment (μ_{eff}(293 K) = 3.9(1) μ_B) is consistent with antiferromagnetic coupling between two ions with S = 1 (Cr^{IV}, d^2) and S = 2 (Cr^{II}, high-spin d^4) ground states. The departure from a symmetrical (Cr(III)$_2$) structure, i.e., the intramolecular disproportionation, may be due to steric interactions between the two nacnac ligands, which prefer a staggered conformation to the eclipsed disposition of the ligands bound to a putative Cr(III)$_2$(μ-O)$_2$ core.

For **3** to be a potential intermediate in the oxygenation of **1**, several conditions have to be met. Obviously, it must react very rapidly with O_2 to produce two equivalents of **2**. Exposure of a THF solution of **3** to O_2 prompted an immediate color change, and the sole product of this reaction was **2**. This reaction is indeed so fast that its rate could not be measured by stopped-flow kinetics even at 203 K, which is consistent with the absence of an observable intermediate during the oxygenation of **1**.

There is, however, a more exacting requirement for the intermediacy of **3**, which affects the outcome of the labeling experiment. Trapping of the initially formed mononuclear dioxygen complex (i.e., **A**) with a second chromium fragment must necessarily yield isotopically homogeneous dinuclear species (e.g., **3**(μ-^{16}O)$_2$ and/or **3**(μ-^{18}O)$_2$). If the subsequent reaction with a second molecule of O_2 is not regioselective, it can easily be shown that the reaction of **1** with a 1:1 $^{16}O_2$/$^{18}O_2$ mixture should yield the three possible isotopologs of the final product (i.e., **2**(^{16}O)$_2$, **2**(^{16}O)(^{18}O), and **2**(^{18}O)$_2$) in a 3:2:3 ratio. As the latter is not the observed result, the oxygenation of **3** must be selective; this is easily tested. Accordingly, **3**(μ-^{16}O)$_2$ was reacted with $^{18}O_2$. MS analysis within 15 min after mixing showed formation of the three isotopologs in the proportion 12:79:9. As this result inevitably includes some contribution of oxygen atom scrambling, it is apparent that the reaction has significant regioselectivity for the formation of only the mixed isotopolog, i.e., **2**(^{16}O)(^{18}O). While this is unusual and we are not sure about the exact mechanism responsible for it, this selectivity is exactly what is required to arrive at the observed 1:2:1 pattern of the original labeling experiment (see Scheme 1).

Scheme 1. Proposed Isotope Labeling Pathways



In aggregate, these observations rule out a mononuclear reaction pathway and provide strong support for the intermediacy of **3** in the oxygenation reaction. However, they do not offer a good rationale for the apparent blockage of the unimolecular transformation of **A** into product **2** by a simple oxidative addition (i.e., O−O bond cleavage). For this we turned to computations.[9]

A mononuclear dioxygen complex **A′** was found to be a minimum on the quartet potential energy surface (PES). Not surprisingly, it represents a Cr(III) peroxo complex, characterized by a pseudotetrahedral coordination of chromium, an O−O distance of 1.459 Å (Cr−O, 1.828 Å), and an O−O stretching frequency of ν_{O-O} = 939 cm^{-1}. The reaction product **2** finds it computational analog in **2′**, a pseudotetrahedral Cr(V) dioxo complex with structural parameters closely related to those of structurally characterized **2** (**2′**: Cr−O, 1.590 Å; Cr−N, 1.957 Å; O−Cr−O, 118.8° vs **2**: Cr−O, 1.591, 1.600 Å; Cr−N, 1.933, 1.936 Å; O−Cr−O, 118.4°).[5] **2′** is a minimum on the doublet PES. It is calculated to be 53 kcal/mol more stable than **A′**; while these calculated energies have considerable uncertainties, there can be no doubt that the transformation from ^{4}**A′** to ^{2}**2′** has a large thermodynamic driving force. However, as is obvious from the above, ^{4}**A′** and ^{2}**2′** have different spin ground states. In other words, the direct conversion is 'spin forbidden'.

The effects of spin-state changes on organometallic and inorganic reactions have been the focus of considerable recent interest.[10] An estimation of the rates of such processes requires the identification of 'minimum energy crossing points'

(MECPs), i.e., energy minima on the seam of intersection between the two relevant PESs. We have employed Harvey's program for locating MECPs;[11] using several different initial geometries—characterized by different O⋯O distances—we have found one MECP (**X′**). The pseudotetrahedral structure of **X′** features an O⋯O distance of 2.022 Å and Cr–O distances of 1.767 Å. **X′** is 17.7 kcal/mol higher in energy than ^{4}**A′** and only 2 kcal/mol below the highest point on the reaction coordinate defined by gradually elongating the O–O bond of the peroxo complex on the quartet PES and leading eventually to an excited state of the product, i.e., ^{4}**2′** (13 kcal/mol below ^{4}**A′** and 40 kcal/mol above ^{2}**2′**).

The picture that emerges of the oxidative addition of the O–O bond of the peroxo ligand to Cr(III) shows that the reaction faces a substantial activation barrier. It is also spin-forbidden, requiring a crossing from a quartet to a doublet PES, resulting in a contribution to the apparent activation entropy. In this case, the MECP is close in energy and structure to the transition state on the quartet PES of the reactant. Either way, the rate of the unimolecular reaction is expected to be relatively slow ($k_1 \sim 10^{-2}$ s^{-1} at RT),[12] which provides ample opportunity for competing, bimolecular pathways to take over.

We are looking for analogous reactions, to ascertain the generality of these observations. However, in the absence of evidence to the contrary, we suggest that the four-electron oxidative addition of O_2 to a single metal center is inherently a slow process and that alternative reaction pathways for the activation of O_2 will generally be favored.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

theopold@udel.edu

Notes

The authors declare no competing financial interest.

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(9) DFT calculation using the B3LYP functional and TZVP basis set were carried out using the program package Gaussian 09. Details are in the SI. For computational economy the aryl groups of the nacnac ligand were replaced with hydrogen atoms; the resulting compounds are labeled with a prime (′).

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(12) Estimated using the Arrhenius equation, with $A = 1 \times 10^{13}$ s^{-1}, $E_a = 17.7$ kcal, and a transmission factor $k = 0.01$.