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O₂ Activation by Non-adiabatic Oxidative Addition to a Single Metal Center

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Abstract

A chromium(I) dinitrogen complex reacts rapidly with O₂ to form the mononuclear dioxo complex Tp^{tBu,Me}Cr^V(O)₂, whereas the analogous reaction with sulfur stops at the persulfido complex Tp^{tBu,Me}Cr^{III}(S₂). The transformation of the putative peroxo intermediate Tp^{tBu,Me}Cr^{III}(O₂)(S = 3/2) into Tp^{tBu,Me}Cr^V(O)₂ (S = 1/2) is spin forbidden. The minimum energy crossing point on the two potential energy surfaces has been identified. While the dinuclear complex (Tp^{tBu,Me}Cr)₂(μ-O)₂ exists, mechanistic experiments suggest that the O₂ activation occurs on a single metal center, by an oxidative addition on the quartet surface followed by crossover to the doublet surface.

TOC image

The 4-electron oxidative addition of O₂ to TpCr(I) is spin forbidden. And yet, it proceeds via a non-adiabatic crossing from a quartet to a doublet potential energy surface at the ‘minimum energy crossing point’ with the structure shown here.

Keywords

Chromium; O-O activation; spin forbidden reaction; sulfur; ab initio calculations

In the context of aerobic oxidations of organic compounds there arises the issue of spin conservation, due to the triplet ground state of dioxygen.^[1] This restriction may be circumvented by the ‘activation’ of O₂ with the aid of metal catalysts.^[2] Thus the formation of dioxygen complexes, and their subsequent transformation into highly reactive metal oxo species has been the focus of intense research interest for many years.^[3] However, both the formation and the transfer of oxo moieties may also involve elementary reactions that are ‘spin forbidden’.^[4] We have been interested in the mechanistic consequences of such occurrences.^[5] Herein we describe the activation of O₂ (and S₈) by low-valent chromium complexes supported by tris(pyrazolyl)borate ligands. Specifically, we suggest that the oxidative addition of O₂ to mononuclear Cr(I) proceeds, despite facing a spin forbidden elementary step.^[6]

We have recently described the synthesis and reactivity of several complexes of chromium in its formal oxidation state +I, including the dinuclear dinitrogen complex [Tp^{Bu,Me}Cr]₂(μ-η¹:η¹-N₂) (**1**) and the even more labile alkyne complex Tp^{Bu,Me}Cr(η²-C₂(SiMe₃)₂) (**2**).^[7] Upon exposure to O₂ gas, cold (−78°C) THF solutions of **1** gradually turned from green to brown, yielding the chromium oxo complex Tp^{Bu,Me}Cr(O)₂ (**3**), i.e., the apparent product of a 4-electron oxidative addition of O₂ to the metal. The structure of **3** is shown in Figure 1a;^[8] it features approximately square pyramidal coordination of chromium, with N5 occupying the apical position. The average Cr–O distance of 1.603(2) Å is in the middle of the range established by chromium oxo complexes.^[9] Befitting its d¹ electronic configuration, the effective magnetic moment of **3** at room temperature was μ_{eff}(RT) = 1.9(1) μ_B. By contrast, the room temperature reaction of **1** with sulfur produced a deep red solution, from which Tp^{Bu,Me}Cr(S₂) (**4**) was isolated in 43% yield. The structure of **4** (see Figure 1b) approximates trigonal bipyramidal coordination of chromium with S1 and N1 occupying the axial positions.^[10] The molecule retains a bond between the two sulfur atoms; at 2.0565(18) Å the S–S distance is consistent with a single bond such as would be expected in a chromium persulfido (S₂^{2−}) ligand.^[11] A band at 541 cm^{−1} in the IR spectrum (KBr) of **4** has been tentatively identified as the S–S stretching frequency (ν_{S–S}) of the ligand. Chromium’s formal oxidation state in **4** is thus +III and the magnetic moment of **4** – μ_{eff}(RT) = 3.7(1) μ_B – is consistent with the quartet ground state of a d³ ion.

The juxtaposition of congeners **3** and **4** is striking, but makes perfect chemical sense. Whereas oxygen is oxidizing enough to stabilize the +V oxidation state of chromium, reaction with the less electronegative sulfur halts at the lesser +III oxidation state of the metal. This explanation is also supported by specific computations. Thus, we have carried out DFT calculations on TpCr(E)₂ and TpCr(E)₂ (Tp = HB(C₃N₂H₃)₃, E = O, S).^[12] We find that the conversion of putative TpCr^{III}(O)₂ to TpCr^V(O)₂ (i.e., **3**′) is exoergic by ΔG = −23.8 kcal/mol, while the analogous transformation of TpCr^{III}(S)₂ (i.e., **4**′) to TpCr^V(S)₂ is thermodynamically unfavorable to the tune of ΔG = +70.8 kcal/mol. Furthermore, we note that the peroxo complex TpCr^{III}(O)₂ (**A**′, tbp geometry, d_{O–O} = 1.464 Å, ν_{O–O} = 908 cm^{−1}, S

= 3/2) is structurally closely related to **4'**. Its physical analog, $\text{Tp}^{\text{Bu,Me}}\text{Cr}(\text{O}_2)$ (**A**), is a prime candidate for an early intermediate in the formation of **3**, and persulfido complex **4** serves as a near perfect model for it.

This is where the spin conservation issue may impact the mechanism of the dioxygen activation! A simple unimolecular O-O bond cleavage suffices to transform **A** into **3**. And yet, the former has a quartet ground state (**4A**) and the latter is a doublet (**23**), rendering this elementary reaction step spin forbidden. The question then is whether this surface crossing is the path of lowest energy or if the reaction proceeds by an alternate – more complicated mechanism. The estimation of the activation barrier and rate of a non-adiabatic reaction transitioning from one potential energy surface (PES) to another involves the identification of ‘minimum energy crossing points’ (MECPs); i.e., the points of lowest energy on the seam forming the intersection of two multidimensional PESs (here the quartet and the doublet state of TpCrO_2). Methods for finding MECPs have been described, and we have used the algorithm developed by Harvey et al.^[13] Starting with a structure intermediate between **4A'** and **23'**, we have located a MECP (**X'**) – see Figure 2. The structure of **X'** features an OÖ distance of 2.363 Å and Cr–O distances of 1.625 and 1.836 Å, and it has an energy only 5.3 kcal/mol above that of **43'**. Thus **X'** is rather product-like. We have also calculated the transition state (**T'**) for the conversion of **4A'** to **43'** on the quartet PES. This reaction has $G^\ddagger = 19.5$ kcal/mol, and the activated complex (OÖ = 1.900 Å, Cr–O_{avg} = 1.765 Å) resembles the reactant more than does **X'**.

In keeping with Harvey’s ‘third rule’, which posits that “for reactions involving a change in atom connectivity as well as a spin state change, the preferred mechanism will usually occur in more than one step, with a spin crossover step preceding or following the bond connectivity change step”,^[4f] we postulate that the oxidative addition of the peroxo ligand of **A** proceeds on the quartet surface, followed by a spin crossover converting **43** into **23**.

A well-precedented mechanistic alternative for the cleavage of O_2 would involve binuclear intermediates. Thus, trapping of **A** with a second equivalent of $\text{Tp}^{\text{Bu,Me}}\text{Cr}^{\text{I}}$ might generate $(\text{Tp}^{\text{Bu,Me}}\text{Cr})_2(\mu\text{-O}_2)$, followed by cleavage of the O-O bond to yield $(\text{Tp}^{\text{Bu,Me}}\text{Cr})_2(\mu\text{-O})_2$ and subsequent reaction with additional O_2 to produce **3**. It was thus of interest to explore the existence of such a binuclear species. Figure 3 shows the product of relevant experiments – e.g., the reaction of **3** with **1**, or the treatment of **1** with only 1.0 equivalent of O_2 or with an excess of N_2O .^[14] $(\text{Tp}^{\text{Bu,Me}}\text{Cr})_2(\mu\text{-O})_2$ (**5**) is a binuclear chromium complex featuring a $\text{Cr}_2(\mu\text{-O})_2$ diamond core, which exhibits significant bond length alternation. Of particular note is the fact that one of the Tp ligands (on Cr2) is coordinated via two pyrazolyl groups and one agostic Cr–H–B interaction – the latter also manifests in a red-shifted $\nu_{\text{B-H}}$ at 2035 cm^{-1} . The likely origin of this rearrangement is severe steric congestion caused by six *tert*-butyl groups brought into close proximity by the close approach of the two metal atoms ($d_{\text{Cr-Cr}} = 2.739(2)$ Å). If nothing else, this might suggest that the formation of **5** faces a significant activation barrier, leaving some room for the unimolecular – albeit spin forbidden alternative. However, **5** reacted with O_2 to yield **3** in good yield; thus a binuclear pathway must be considered viable.

Faced with a similar mechanistic question in the oxygenation of (*i*-Pr₂Ph)₂nacnacCr(η²-C₂(SiMe₃)₂), we had turned to ¹⁶O/¹⁸O isotope labeling studies to provide strong evidence that the reaction proceeded via a binuclear intermediate.^[5d] Unfortunately this proved impossible here, as a control experiment with an equimolar mixture of **3**-¹⁶O₂ and **3**-¹⁸O₂ resulted in rapid isotope scrambling, presumably via a dinuclear intermediate of the type TpCr(O)(μ-O)₂(O)CrTp. Searching for other incisive mechanistic experiments, we reasoned that the binuclear pathway depends critically on the availability of substitutionally labile Tp^tBu,MeCr^I fragments to trap the initially formed **A**. Therefore, if a reaction could be devised to generate **A** in the absence of the former, a distinction might be made. To this end we have used the previously prepared chromium superoxo complex Tp^tBu,MeCr(O₂)Cl.^[15] K₂C₈ reduction of this complex in THF at -35°C effected a rapid color change from red to brown, and work-up of the solution yielded crystalline **3** in 77 % isolated yield. We propose that reduction of Tp^tBu,MeCr(O₂)Cl caused loss of chloride with concomitant formation of Tp^tBu,MeCr(O₂) (i.e., **A**, in which the erstwhile superoxo ligand has been reduced to a peroxo moiety), but in the absence of coordinatively unsaturated chromium and thus unable to form a binuclear compound. The ready production of **3** in high yield under these conditions then argues strongly that the unimolecular rearrangement of **4A** to **23** is indeed facile.

In summary, we have investigated – experimentally and computationally – the 4-electron oxidative addition of O₂ to a labile TpCr(I) precursor. The preponderance of the evidence suggests that in this system the unimolecular transformation of a Cr(III) peroxo intermediate (**A**) to the isomeric Cr(V) dioxo product (**3**) – while spin forbidden – is nevertheless the prevailing mechanistic pathway. We conclude that the effects of spin conservation on the mechanism of inorganic reactions are variable and require case-by-case evaluation. In other words, ‘spin forbidden’ reaction may indeed face particular constraints, but they cannot be ruled out categorically.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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8. $C_{48}H_{80}B_2Cr_2N_{12}O_2$, $M_r = 982.86$, crystal dimensions = $0.339 \times 0.241 \times 0.237$ mm, monoclinic $P2_1/c$, $a = 20.7125(7)$, $b = 14.7706(5)$, $c = 22.5952(8)$ Å, $\beta = 103.7730(10)^\circ$, $V = 6713.9(4)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 0.972$ g cm⁻³, $\mu = 0.362$ mm⁻¹, Mo-K α $\lambda = 0.71073$ Å, $T = 200(2)$ K, $2\theta_{\text{max}} = 55.0$, 86171 reflections measured, 15408 independent reflections, $R_{\text{int}} = 0.0536$, $R_1 = 0.0558$, $wR_2 = 0.1435$, residual electron density = 0.802 e Å⁻³. The t-butyl group on the noncoordinated pyrazole was located disordered in two positions with a refined site occupancy of 58/42. Two disordered pentane molecules of solvation per compound molecule were treated as diffused contributions. Borohydride H-atoms located from difference map. CCDC number: 1414458.
9. A search of CSD revealed 288 complexes with terminal oxo ligands coordinated to Cr. 4 of these were eliminated as outliers, leaving 781 Cr=O bonds. Their mean Cr-O distance was 1.604(31) Å.
10. $C_{32}H_{56}BCrN_6O_2S_2$, $M_r = 683.75$, crystal dimensions = $0.438 \times 0.388 \times 0.364$ mm, orthorhombic $Pnma$, $a = 18.487(14)$, $b = 21.314(16)$, $c = 9.395(7)$ Å, $V = 3702(5)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.227$ g cm⁻³, $\mu = 0.458$ mm⁻¹, Mo-K α $\lambda = 0.71073$ Å, $T = 200(2)$ K, $2\theta_{\text{max}} = 56.8$, 48217 reflections measured, 4723 independent reflections, $R_{\text{int}} = 0.0418$, $R_1 = 0.0405$, $wR_2 = 0.1201$, residual electron density = 0.640 e Å⁻³. Compound molecule resides on a mirror plane. THF solvent molecule treated with rigid bond restraints. CCDC number: 1414459.
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12. DFT calculations using the B3LYP functional and TZVP basis set were carried out using the program package Gaussian 09. Details are in the ESI. For computational economy the alkyl substituents of the Tp ligands were replaced with hydrogen atoms; the resulting compounds are labeled with a prime (').
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14. $C_{24}H_{40}BCrN_6O_2$, $M_r = 507.43$, crystal dimensions = $0.274 \times 0.271 \times 0.150$ mm, monoclinic $P2_1/n$, $a = 9.309(3)$, $b = 30.574(10)$, $c = 9.374(3)$ Å, $\beta = 101.167(6)^\circ$, $V = 2617.4(14)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.288$ g cm⁻³, $\mu = 0.467$ mm⁻¹, Mo-K α $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{\text{max}} = 55.0$, 24396 reflections measured, 6001 independent reflections, $R_{\text{int}} = 0.0773$, $R_1 = 0.0514$, $wR_2 = 0.1296$, residual electron density = 0.333 e Å⁻³. CCDC number: 1414460.
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Figure 1.

Molecular structures of a) **3** and b) **4** (30 % probability level). Selected interatomic distances (Å) and angles(°): a) Cr–O1, 1.6007(19); Cr–O2, 1.6050(19); Cr–N1, 2.216(2); Cr–N3, 2.265(2); Cr–N5(1.979(2); O1–Cr–O2, 108.14(10); b) Cr–S1, 2.3220(15); Cr–S2, 2.2398(16); S1–S2, 2.0565(18), Cr–N_{avg}, 2.109; S1–Cr–S2, 53.55(6).

Figure 2.

Reaction coordinate diagram for the 'spin forbidden' transformation of **A** into **3**. Structures shown are those calculated with DFT, showing the evolution of the OÖ distance.

Figure 3.

The molecular structure of binuclear **5** (30% probability level). Selected interatomic distances (Å) and angle (°): Cr1–O1, 1.9203(15); Cr1–O2, 1.7871(15); Cr2–O1, 1.7608(15); Cr2–O2, 1.8924(15); Cr1–NTp,avg, 2.158; Cr2–NTp,avg, 2.154; Cr2–H2B, 1.78(2); O1–Cr1–O2, 82.38(7); O1–Cr2–O2, 83.88(7); Cr1–O1–Cr2, 96.07(7); Cr1–O2–Cr2, 96.18(7).