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Spin-Forbidden Reactions **Hot Paper**

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Dioxygen Activation by Non-Adiabatic Oxidative Addition to a Single Metal Center

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Abstract: *A chromium(I) dinitrogen complex reacts rapidly with O_2 to form the mononuclear dioxo complex [$Tp^{tBu,Me}Cr^{V}(O)_2$] ($Tp^{tBu,Me}$ = hydrotris(3-tert-butyl-5-methylpyrazolyl)borate), whereas the analogous reaction with sulfur stops at the persulfido complex [$Tp^{tBu,Me}Cr^{III}(S_2)$]. The transformation of the putative peroxo intermediate [$Tp^{tBu,Me}Cr^{III}(O_2)$] ($S = ^3/_2$) into [$Tp^{tBu,Me}Cr^{V}(O)_2$] ($S = ^1/_2$) is spin-forbidden. The minimum-energy crossing point for the two potential energy surfaces has been identified. Although the dinuclear complex [$(Tp^{tBu,Me}Cr)_2(\mu\text{-}O)_2$] exists, mechanistic experiments suggest that O_2 activation occurs on a single metal center, by an oxidative addition on the quartet surface followed by crossover to the doublet surface.*

In the context of aerobic oxidations of organic compounds, the issue of spin conservation arises, owing to the triplet ground state of dioxygen.[1] This restriction may be circumvented by the "activation" of O_2 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 O_2 (and S_8) by low-valent chromium complexes supported by tris(pyrazolyl)borate ligands. Specifically, we suggest that the oxidative addition of O_2 to mononuclear chromium(I) proceeds, despite facing a spin-forbidden elementary step.[6]

We recently described the synthesis and reactivity of several complexes of chromium in its formal oxidation state +I, including the dinuclear dinitrogen complex [$(Tp^{tBu,Me}Cr)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)$] (**1**; $Tp^{tBu,Me}$ = hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate) and the even more labile alkyne complex [$Tp^{tBu,Me}Cr(\eta^2\text{-}C_2(SiMe_3)_2)$] (**2**).[7] Upon exposure to O_2 gas, cold (−78 °C) THF solutions of **1** gradually turned from green to brown, yielding the chromium oxo complex [$Tp^{tBu,Me}Cr(O)_2$] (**3**), the apparent product of a four-electron oxidative addition of O_2 to the metal. The structure of **3** is shown in Figure 1 (top);[8] it features approximately square-pyramidal coordination of chromium, with the N5 nitrogen atom occupying the apical position. The average Cr−O distance of 1.603(2) Å is in the middle of the range established for chromium oxo complexes.[9] Befitting its d^1 electronic configuration, the effective magnetic moment of **3** at room temperature was $\mu_{eff}(RT) = 1.9(1)\ \mu_B$. By contrast, the room-temperature reaction of **1** with sulfur produced a deep red solution, from which [$Tp^{tBu,Me}Cr(S_2)$] (**4**) was isolated in 43 % yield. The structure of **4** (see Figure 1, bottom) approximates trigonal-bipyramidal coordination of chromium with the S1 and N1 atoms 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 (S_2^{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 fre-

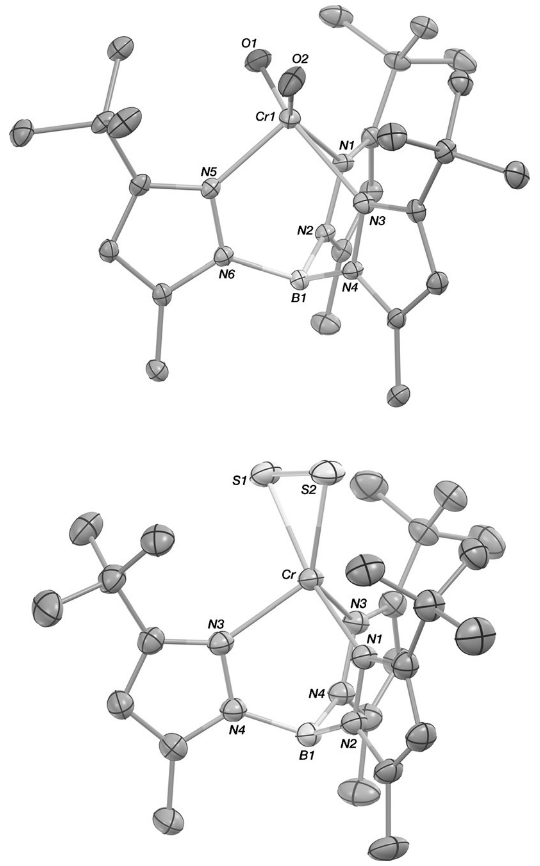

Figure 1. Molecular structures of a) **3** and b) **4** (ellipsoids set at 30% probability). Selected interatomic distances [Å] and angles [°]: a) Cr–O1 1.6007(19), Cr–O2 1.6050(19), Cr–N1 2.216(2); Cr–N3 2.265(2), Cr–N5 1.979(2); O1-Cr-O2 108.14(10); b) Cr–S1 2.3220(15), Cr–S2 2.2398(16), S1–S2 2.0565(18), Cr–N (avg.) 2.109; S1-Cr-S2 53.55(6).

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quency (ν_{S-S}) of the ligand. The formal oxidation state of chromium in **4** is thus +III, and the magnetic moment of **4**, $\mu_{eff}(RT) = 3.7(1)\ \mu_B$, is consistent with the quartet ground state of a d^3 ion.

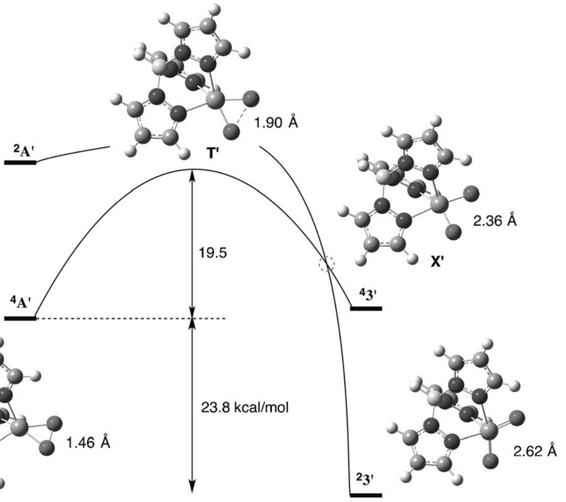

Figure 2. Reaction coordinate diagram for the spin-forbidden transformation of **A** into **3**. The structures shown are those calculated by DFT, showing the evolution of the O⋯O distance.

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 was also supported by specific computations. Thus we have carried out DFT calculations on $[TpCr(E_2)]$ and $[TpCr(E)_2]$ ($Tp = HB(C_3N_2H_3)_3$, E = O, S).[12] The conversion of putative $[TpCr^{III}(O_2)]$ into $[TpCr^{V}(O)_2]$ (i.e., **3′**) was found to be exoergic by $\Delta G = -23.8\ kcal\,mol^{-1}$, whereas the analogous transformation of $[TpCr^{III}(S_2)]$ (i.e., **4′**) into $[TpCr^{V}(S)_2]$ is thermodynamically unfavorable with $\Delta G = +70.8\ kcal\,mol^{-1}$. Furthermore, the peroxo complex $[TpCr^{III}(O_2)]$ (**A′**, tbp geometry, $d_{O-O} = 1.464$ Å, $\nu_{O-O} = 908\ cm^{-1}$, $S = 3/2$) is structurally closely related to **4′**. Its physical analogue, $[Tp^{tBu,Me}Cr(O_2)]$ (**A**), is a prime candidate for an early intermediate in the formation of **3**, and persulfido complex **4** serves as a nearly 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 (^{4}**A**) and the latter is a doublet (^{2}**3**), 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), which are the points of lowest energy on the seam forming the intersection of two multi-dimensional 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 ^{4}**A′** and ^{2}**3′**, we have located an MECP (**X′**; see Figure 2). The structure of **X′** features an O⋯O distance of 2.363 Å and Cr−O distances of 1.625 and 1.836 Å, and it has an energy only $5.3\ kcal\,mol^{-1}$ above that of ^{4}**3′**. Therefore, **X′** is rather product-like. We have also calculated the transition state (**T′**) for the conversion of ^{4}**A′** into ^{4}**3′** on the quartet PES. This reaction has $\Delta G^{\neq} = 19.5\ kcal\,mol^{-1}$, and the activated complex (O⋯O = 1.900 Å, average Cr−O = 1.765 Å) resembles the reactant more than does **X′**.

In keeping with Harvey's "third rule", which states 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 ^{4}**3** into ^{2}**3**.

A well-precedented mechanistic alternative for the cleavage of O_2 would involve binuclear intermediates. Thus, trapping of **A** with a second equivalent of $[Tp^{tBu,Me}Cr^{I}]$ might generate $[(Tp^{tBu,Me}Cr)_2(\mu\text{-}O_2)]$, followed by cleavage of the O−O bond to yield $[(Tp^{tBu,Me}Cr)_2(\mu\text{-}O)_2]$ 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, namely the reaction of **3** with **1** or the treatment of **1** with only one equivalent of O_2 or with an excess of N_2O.[14] $[(Tp^{tBu,Me}Cr)_2(\mu\text{-}O)_2]$ (**5**) is a binuclear chromium complex featuring a $\{Cr_2(\mu\text{-}O)_2\}$ 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 itself in a red-shifted ν_{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 ($d_{Cr-Cr} = 2.739(2)$ Å). If

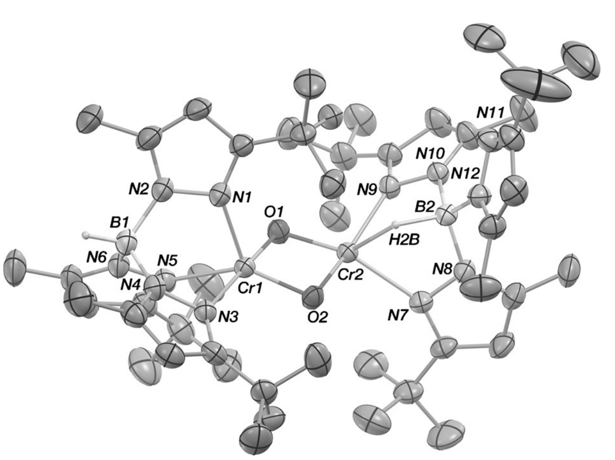

Figure 3. Molecular structure of binuclear **5** (ellipsoids set at 30% probability). Selected interatomic distances [Å] and angles [°]: Cr1–O1 1.9203(15), Cr1–O2 1.7871(15), Cr2–O1 1.7608(15), Cr2–O2 1.8924(15), Cr1–N_{Tp} (avg.) 2.158, Cr2–N_{Tp} (avg.) 2.154, Cr2–H2B 1.78(2); O1-Cr1-O2 82.38(7), O1-Cr2-O2 83.88(7), Cr1-O1-Cr2 96.07(7), Cr1-O2-Cr2 96.18(7).

nothing else, this might suggest that the formation of **5** faces a significant activation barrier, leaving some room for the unimolecular, 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 [$(i\mathrm{Pr}_2\mathrm{Ph})_2$nacnacCr($\eta^2$-$C_2(SiMe_3)_2$)] (nacnac = β-diketiminate), we had turned to $^{16}O/^{18}O$ 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 [$^{16}O_2$]-**3** and [$^{18}O_2$]-**3** 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 {$\mathrm{Tp}^{t\mathrm{Bu,Me}}\mathrm{Cr}^{\mathrm{I}}$} fragments to trap 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 used the previously prepared chromium superoxo complex [$\mathrm{Tp}^{t\mathrm{Bu,Me}}\mathrm{Cr(O_2)Cl}$].[15] KC_8 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 % yield. We propose that reduction of [$\mathrm{Tp}^{t\mathrm{Bu,Me}}\mathrm{Cr(O_2)Cl}$] caused loss of chloride with concomitant formation of [$\mathrm{Tp}^{t\mathrm{Bu,Me}}\mathrm{Cr(O_2)}$] (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 is 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 **^{4}A** into **^{2}3** is indeed facile.

In summary, we have investigated, both experimentally and computationally, the four-electron oxidative addition of O_2 to a labile $\mathrm{TpCr^I}$ precursor. The results suggest that in this system, the unimolecular transformation of a $\mathrm{Cr^{III}}$ peroxo intermediate (**A**) into the isomeric $\mathrm{Cr^V}$ 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" reactions may indeed face particular constraints, but they cannot be ruled out categorically.

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Keywords: ab initio calculations · chromium · dioxygen activation · spin-forbidden reactions · sulfur

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[8] $C_{48}H_{80}B_2Cr_2N_{12}O_2$, $M_r = 982.86$, crystal dimensions = 0.339 mm × 0.241 mm × 0.237 mm, monoclinic $P2_1/c$, $a = 20.7125(7)$, $b = 14.7706(5)$, $c = 22.5952(8)$ Å, $\beta = 103.7730(10)°$, $V = 6713.9(4)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 0.972$ g cm^{-3}, $\mu = 0.362$ mm^{-1}, Mo-kα: $\lambda = 0.71073$ Å, $T = 200(2)$ K, $2\theta_{\max} = 55.0$, 86171 reflections measured, 15408 independent reflections, $R_{\mathrm{int}} = 0.0536$, $R_1 = 0.0558$, $wR_2 = 0.1435$, residual electron density = 0.802 e Å^{-3}. The *tert*-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 hydrogen atoms located from difference map. CCDC 1414458 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[9] A search of the Cambridge Structural Database revealed 288 complexes with terminal oxo ligands coordinated to Cr. Four 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 mm × 0.388 mm × 0.364 mm, orthorhombic *Pnma*, $a = 18.487(14)$, $b = 21.314(16)$, $c = 9.395(7)$ Å, $V = 3702(5)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.227$ g cm^{-3}, $\mu = 0.458$ mm^{-1}, Mo-kα: $\lambda = 0.71073$ Å, $T = 200(2)$ K, $2\theta_{\max} = 56.8$, 48217 reflections measured, 4723 independent reflections, $R_{\mathrm{int}} = 0.0418$, $R_1 = 0.0405$, $wR_2 = 0.1201$, residual electron density = 0.640 e Å^{-3}. Compound molecule resides on a mirror plane. THF solvent molecule treated with rigid bond restraints. CCDC 1414459 contains the supplementary crystallo-

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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 given in the Supportin Information. 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 mm × 0.271 mm × 0.150 mm, monoclinic $P2_1/n$, $a = 9.309(3)$, $b = 30.574(10)$, $c = 9.374(3)$ Å, $\beta = 101.167(6)°$, $V = 2617.4(14)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.288$ g cm^{-3}, $\mu = 0.467$ mm^{-1}, Mo-kα: $\lambda = 0.71073$ 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 1414460 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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