Hydrogen Tunneling in the Activation of Dioxygen by a Tris(pyrazolyl)borate Cobalt Complex

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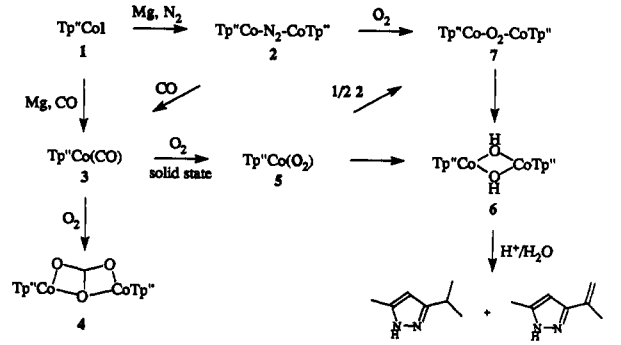
The activation of dioxygen by coordination to metals plays an important role in living organisms as well as artificial oxidation catalysts.[1] Detailed mechanistic understanding of this process must rely on structural characterization of reactive intermediates and elucidation of their reaction pathways. However, the conflicting demands of high reactivity—for catalysis—and stability sufficient for characterization have proven challenging.

We have previously described the dioxygen complex Tp′$Co^{II}(O_2)$ (Tp′ = hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borate) and its reaction with Tp′$Co^{I}(N_2)$ to yield Tp′$Co^{II}OH$, the apparent product of hydrogen atom abstraction by a highly reactive cobalt–oxo complex.[2] Herein we report related chemistry of the Tp″Co-moiety (Tp″ = hydridotris(3-isopropyl-5-methylpyrazolyl)-borate),[3] including the observation of an intermediate and evidence for a tunneling contribution to hydrogen atom abstraction from the ligand.

Mg reduction of Tp″Co^{II}I (**1**)[4] in THF under N_2 yielded the dinitrogen complex [(Tp″Co^{I})$_2$(μ-N_2)] (**2**[5], see Scheme 1). The lesser steric demand of the isopropyl substituents of the Tp″ ligand apparently favors the dinuclear structure, in contrast to mononuclear Tp′Co(N_2).[2] Similarly, reduction under CO produced the carbonyl complex Tp″Co^{I}(CO) (**3**).[6] Attempts to prepare Tp″Co(O_2) by oxygenation of solutions of either **2** or **3** failed. Indeed, the isolation of the carbonate complex [(Tp″Co^{II})$_2$(μ-η^2,η^2-CO_3)] (**4**)[7] from the reaction of **3** with O_2 was another indication of the significant difference between the Tp″ and Tp′ ligands. However, reasoning that the formation of **4** might reflect trapping of the desired Tp″Co(O_2) by remaining **3** in a bimolecular reaction, we sought to eliminate the latter. Thus, exposure of

Scheme 1



solid **3** to 0.8 atm of O_2 for 24 h produced pure Tp″$Co^{II}(O_2)$ (**5**)[8] in quantitative yield. Based on the analytical data and the close similarity of its spectroscopic properties to Tp′Co(O_2),[2] we believe **5** to be an analogue of the latter, i.e., a tetrahedral Co^{II} superoxide complex featuring a side-on bound O_2 ligand.

Although stable in the solid state, Tp″Co(O_2) decomposed in solution with concomitant release of 0.47(4) equiv of O_2 (measured with a Töpler pump). The ^{1}H NMR spectrum of the final decomposition product showed the formation of the hydroxide complex [(Tp″Co^{II})$_2$(μ-OH)$_2$] (**6**)[9] in ca. 45% yield, along with other uncharacterized paramagnetic species. Acid hydrolysis of this mixture (0.5 N H_2SO_4, 2 h reflux), followed by addition of excess NH_3(aq) and extraction with ether, yielded a mixture of two pyrazoles, namely 3-isopropyl-5-methylpyrazole and 3-isopropenyl-5-methylpyrazole in a ratio of 9:1 (see Scheme 1). The dehydrogenated pyrazole was identified by comparison with an independently prepared sample.[10]

Monitoring of the thermal decomposition of Tp″Co(O_2) by ^{1}H NMR (CD_2Cl_2) revealed the formation of a transient intermediate. Pure samples of the same complex were formed upon exposure of **2** (solid or in solution) to O_2 (0.8 atm, –78 °C). Finally, the intermediate could also be prepared cleanly by the low-temperature reaction of Tp″Co(O_2) with 0.5 equiv of **2**. Based on these observations, we assign to the intermediate the structure [(Tp″Co^{II})$_2$(μ-O_2)] (**7**).[11] **7** is closely related to Kitajima's [Cu(HB(3,5-iPr$_2$pz)$_3$)]$_2$(μ-O_2),[12] and we are trying to grow crystals for a structure determination. Upon warming of **7** (solid or in solution) to ambient temperature, it rapidly decomposed, yielding the same mixture of decomposition products obtained from **5**.

Due to the importance of **7** to the O_2-activation and ligand functionalization step, a kinetic study and determination of the activation parameters for its reaction were of interest. The

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(5) [(Tp″Co)$_2$(μ-N_2)] (**2**): ^{1}H NMR (C_6D_6) δ –12.1 (3 H), –7.2 (18 H), 21.3 (9 H), 32.4 (1 H), 54.4 (3 H); IR (KBr) 2511 (ν_{BH}), 2052 (ν_{NN}) cm^{-1}; UV/vis/NIR (toluene) 380 (sh, ϵ = 2800), 790 (ϵ = 420), 1000 (ϵ = 360), 1640 (ϵ = 110) nm; mp 220 °C dec. Anal. Calcd for $C_{42}H_{68}B_2Co_2N_{14}$: C, 55.52; H, 7.79; N, 21.58. Found: C, 55.93; H, 7.79; N, 21.58. μ_{eff}(room temperature) = 5.6 μ_B (4.0 μ_B/Co). The crystal structures of **2**, **4**, and **6** have been determined and will be described in the full paper.

(6) Tp″Co(CO) (**3**): ^{1}H NMR (C_6D_6) δ –10.3 (3 H), –6.1 (18 H), 18.4 (9 H), 22.4 (1 H), 34.1 (3 H); IR (KBr) 2525 (ν_{BH}), 1940 (ν_{CO}) cm^{-1}; UV/vis/NIR (THF) 659 (ϵ = 140), 659 (ϵ = 140), 1126 (ϵ = 180) nm; mp 196 °C. Anal. Calcd for $C_{22}H_{34}BCoN_6O$: C, 56.43; H, 7.32; N, 17.95. Found: C, 56.09; H, 7.23; N, 17.43. μ_{eff}(room temperature) = 3.1 μ_B.

(7) [(Tp″Co)$_2$(μ-η^2,η^2-CO_3)] (**4**): ^{1}H NMR (C_6D_6) δ –68.0 (3 H), –23.8 (18 H), 33.3 (9 H), 44.9 (3 H), 71.3 (1 H); IR (KBr) 2522 (ν_{BH}), 1558 (ν_{CO}) cm^{-1}; UV/vis/NIR (C_6H_6) 300 (sh, ϵ = 1000), 479 (sh, ϵ = 145), 540 (sh, ϵ = 180), 573 (ϵ = 105), 722 (sh, ϵ = 20), 1012 (sh, ϵ = 12) nm; mp 222 °C. Anal. Calcd for $C_{43}H_{68}B_2Co_2N_{12}O_3$: C, 54.91; H, 7.29; N, 17.87. Found: C, 54.95; H, 7.49; N, 17.89. μ_{eff}(room temperature) = 6.5 μ_B (4.6 μ_B/Co).

(8) Tp″Co(O_2) (**5**): ^{1}H NMR (CD_2Cl_2) δ –8.84 (3 H), –5.35 (18 H), 16.2 (1 H), 22.24 (9 H), 34.11 (3 H); IR (KBr) 2524 (ν_{BH}), 941 ($\nu_{^{16}O^{16}O}$), 890 ($\nu_{^{18}O^{18}O}$) cm^{-1}; UV/vis/NIR (CH_2Cl_2) 325 (sh, ϵ = 1600), 753 (ϵ = 260), 978 (ϵ = 240) nm; mp 136 °C dec. Anal. Calcd for $C_{21}H_{34}BCoN_6O_2$: C, 53.41; H, 7.26; N, 17.79. Found: C, 53.60; H, 7.26; N, 17.64. μ_{eff}(room temperature) = 3.3 μ_B.

(9) [(Tp″Co)$_2$(μ-OH)$_2$] (**6**): ^{1}H NMR (CD_2Cl_2) δ –143.7 (3 H), –56.0 (18 H), 51.4 (3 H), 65.2 (9 H), 163.9 (1 H); IR (KBr) 3707 (ν_{OH}), 2734 (ν_{OD}), 2525 (ν_{BH}) cm^{-1}; UV/vis/NIR (C_6H_6) 452 (ϵ = 65), 527 (ϵ = 40), 723 (ϵ = 22), 1009 (ϵ = 12) nm; mp 258 °C dec. Anal. Calcd for $C_{42}H_{70}B_2Co_2N_{12}O_2$: C, 55.15; H, 7.71; N, 18.38. Found: C, 55.09; H, 7.69; N, 18.43. μ_{eff}(room temperature) = 6.9 μ_B (4.9 μ_B/Co).

(10) 3-Isopropenyl-5-methylpyrazole: ^{1}H NMR (C_6D_6) δ 1.93 (d, 3 H, J = 0.5 Hz), 2.07 (dd, 3 H, J = 0.9, 1.4 Hz), 4.96 (dq, 1 H, J = 1.4 Hz), 5.48 (dq, 1 H, J = 1.4 Hz, J = 0.9 Hz), 5.94 (d, 1 H, J = 0.5 Hz), 10.40 (br s, 1 H); ^{13}C NMR (C_6D_6) δ 11.57, 20.62 (2 CH_3), 102.03 (CH), 111.78 (CH_2), 135.97, 143.12, 150.04 (3 C_{quat}); mp 63 °C; HRMS *m/e* 122.0841 (M^+, calcd for $C_7H_{10}N_2$ 122.0844).

(11) [(Tp″Co)$_2$(μ-O_2)] (**7**): ^{1}H NMR (CD_2Cl_2, –25 °C) δ –20.7 (3 H), –5.9 (18 H), 7.2 (3 H), 9.7 (9 H), 24.2 (1 H); UV/vis/NIR (toluene) 474 (sh), 670 (ϵ = 540), 810 (ϵ = 170), 1480 (ϵ = 20) nm.

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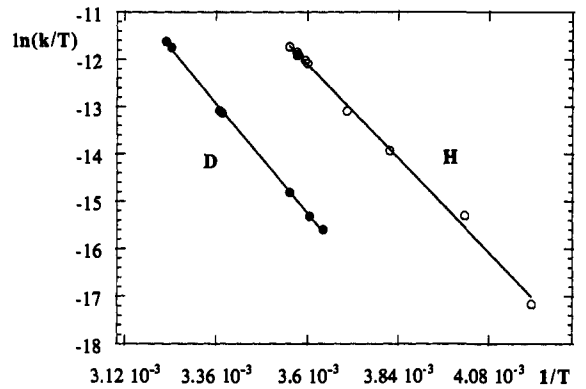
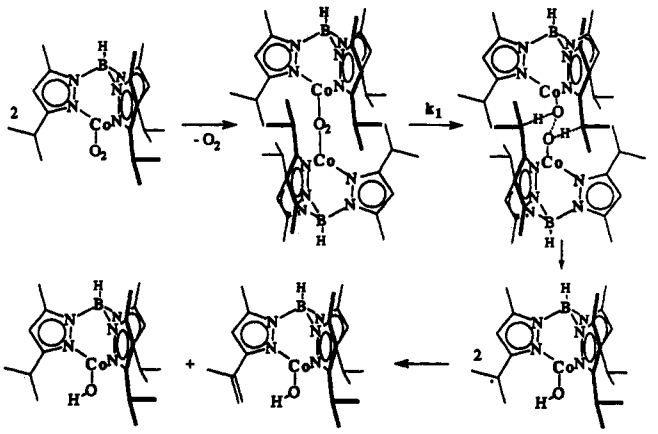


Figure 1. Eyring plot for the decomposition reactions of $[(Tp''Co)_2(\mu\text{-}O_2)]$ (H) and $[(Tp''\text{-}d_{15})_2(\mu\text{-}O_2)]$ (D). The activation parameters are for H, $\Delta H^{\ddagger} = 16.4(5)$ kcal/mol, $\Delta S^{\ddagger} = -12(1)$ eu; for D, $\Delta H^{\ddagger} = 19.2(5)$ kcal/mol, $\Delta S^{\ddagger} = -8(1)$ eu. An Arrhenius analysis of the same rate data gave, for H, $E_a = 17.0$ kcal/mol, $A_H = 3.4 \times 10^{10}$ s^{-1}; for D, $E_a = 19.8$ kcal/mol, $A_D = 2.6 \times 10^{11}$ s^{-1}.

decomposition of $[(Tp''Co)_2(\mu\text{-}O_2)]$ in CD_2Cl_2 was monitored by ^{1}H NMR; it followed first-order kinetics with $k_1(281\ K) = 2.27(3) \times 10^{-3}$ s^{-1}. The Eyring analysis of rate constants determined in the range 238–281 K gave $\Delta H^{\ddagger} = 16.4(5)$ kcal/mol and $\Delta S^{\ddagger} = -12(1)$ eu (see Figure 1). The reaction showed no significant dependence on solvent polarity (i.e., $k_1(281\ K$, toluene$) = 1.6 \times 10^{-3}$ s^{-1} and $k_1(281$ K, acetonitrile$) = 2.5 \times 10^{-3}$ s^{-1}). The negative activation entropy of this reaction argued against a simple O–O bond dissociation in the rate-determining step. In order to check for involvement of C–H bond breaking, we have carried out isotope effect measurements. H/D exchange of the pyrazole precursor (i.e., 5-methyl-2,4-hexanedione) facilitated preparation of 7-d_{30}, carrying deuterium—inter alia—in the tertiary positions of the isopropyl groups. The rate of decomposition of 7-d_{30} at 281 K was $1.04(5) \times 10^{-4}$ s^{-1}, giving $k_H/k_D(281\ K) = 22(1)$. While such an unusually large kinetic isotope effect might be explained as resulting from a concerted abstraction of two hydrogen/deuterium atoms in the rate-determining step, the possibility of a tunneling contribution to the reaction had to be considered. Four criteria are commonly used to establish quantum mechanical tunneling in a hydrogen-transfer reaction:[13] (1) large kinetic isotope effects ($k_H/k_D \gg 7$ at room temperature), (2) curvature in the Eyring plot (i.e., the appearance of a temperature-independent contribution to the reaction rate at low temperatures), (3) difference in the apparent activation enthalpies exceeding the zero-point energy differences of the C–H and C–D bonds ($\Delta(\Delta H^{\ddagger}) > 1.3$ kcal/mol), (4) difference in the preexponential factors (A-factors) resulting from an Arrhenius analysis ($A_H/A_D < 0.6$; in the Eyring analysis this appears as a difference in $\Delta S^{\ddagger}$). Figure 1 shows a comparative Eyring plot for the decompositions of 7 and 7-d_{30}. The experimentally accessible temperature range of rate constants was not large enough to establish nonlinearity; however, the $\Delta(\Delta H^{\ddagger})$ of 2.8 kcal/mol is just larger than the sum of zero-point energy differences of two C–H(D) bonds. The activation entropies differ significantly; a parallel Arrhenius analysis of the data yielded $A_H/A_D = 0.13$. We conclude that the rate-determining step of the decomposition of the binuclear dioxygen complex 7 involves C–H bond breaking and that the hydrogen transfer probably involves tunneling. Recently, tunneling has been proposed to be a general feature of enzymatic hydrogen-transfer reactions,[14] possibly including the alkane hydroxylation catalyzed by methane monooxygenase.[15] The system described above may thus serve as a functional model of certain biological reaction steps.

Scheme 2



Scheme 2 shows a proposed mechanism for the cobalt-mediated activation of the dioxygen molecule, consistent with our observations. Binding of O_2 to one metal center reduces the former to superoxide. Association of a second metal center then yields a μ-peroxo complex. Its O–O bond is expected to be weak, and homolytic rupture would produce a cobalt–oxo moiety (i.e., Tp''Co(O$^{\bullet}$)). No stable example of such a complex is presently known,[16] and its actual formation may be circumvented by concomitant O–O/C–H bond breaking and O–H bond making. The absence of a significant solvent effect on the reaction rate militates against a heterolytic cleavage of the O–O bond though. A picture of the highly ordered transition structure, which provides an explanation for the negative $\Delta S^{\ddagger}$, is shown in Scheme 2. Hydrogen atom abstraction from the isopropyl groups of the Tp'' ligands generates alkyl radicals, which proceed via disproportionation to isopropyl and isopropenyl substituents in the hydroxide complex. Thus the Tp''Co system provides a unique opportunity to directly observe the binding of O_2 and its subsequent transformation into a ligand, which is capable of attacking C–H bonds.

We have designed and synthesized a metal complex which enables the direct observation of individual steps in the activation of dioxygen toward the functionalization of C–H bonds. Further work will involve detailed structural and mechanistic studies of this system as well as modifications aimed at catalytic functionalizations of hydrocarbons with O_2.

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Supplementary Material Available: Representative kinetics plots and rate data (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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