

Hydrogen Atom Abstraction by a Chromium(IV) Oxo Complex Derived from O₂

Kun Qin, Christopher D. Incarvito, Arnold L. Rheingold, and Klaus H. Theopold*

Department of Chemistry and Biochemistry, Center for Catalytic Science and Technology, University of Delaware, Newark, Delaware 19716

Received September 3, 2002

Hydrogen atom abstraction from organic substrates by metal-oxo species derived from O₂ constitutes a reactivity paradigm of bioinorganic chemistry and oxidation catalysis.¹ We and others have previously described the synthesis of cobalt dioxygen complexes that give rise to reactive intermediates of the type Tp^{R,R}Co=O or Tp^{R,R}Co(μ-O)₂CoTp^{R,R}.² The recent advent of a series of closely related chromium dioxygen complexes has presented us with the opportunity to investigate analogous chemistry of an early transition metal.³ Chromium-oxo complexes should be more stable and might thus serve as models for the more elusive intermediates in cobalt chemistry.⁴

To our surprise, reaction of the superoxo complex [Tp^{Bu,Me}Cr(κ²-O₂)(pz'H)]BARF (Tp^{Bu,Me} = hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate, pz'H = 3-*tert*-butyl-5-methylpyrazole, BARF = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate)³ with [Tp^{Bu,Me}Cr(pz'H)]BARF in Et₂O at room temperature produced the brown hydroxide [Tp^{Bu,Me}Cr(OH)(pz'H)]BARF (**1**) in excellent yield. The IR spectrum (KBr) of **1** showed two distinct bands at 3669 cm⁻¹ (ν_{O-H}) and 3298 cm⁻¹ (ν_{N-H}), and the magnetic moment of **1** (μ_{eff} (295 K) = 3.7(1) μ_B) was consistent with a Cr(III) complex (d³, S = 3/2). The molecular structure of **1** (see Figure 1) confirmed the structural assignment.⁵

1 adopts a distorted trigonal bipyramidal geometry, with N(3) and N(7) occupying the axial positions. The Cr–O distance of 1.814(2) Å is consistent with a single bond, and the hydrogen atoms of the hydroxide and pyrazole ligands were both located crystallographically.⁶

The formation of Cr(III) hydroxide **1** instead of the expected Cr(IV) oxo complex resembles the outcome of the reaction of Tp^{Bu,Me}Co(O₂) with Tp^{Bu,Me}Co(N₂), which yielded Tp^{Bu,Me}CoOH.^{2a} A reactive metal-oxo species is a probable intermediate in both cases. Consistent with this hypothesis, **1** could also be prepared by reaction of [Tp^{Bu,Me}Cr(pz'H)]BARF with oxygen atom donors such as trimethylamine-*N*-oxide or iodosylbenzene in Et₂O. Thus, we propose that [Tp^{Bu,Me}Cr(O)(pz'H)]BARF (**2**) arises as an intermediate in the formation of **1**, followed by hydrogen atom abstraction (see Scheme 1).¹ This proposal is noteworthy in light of the apparent stability of the closely related Tp^{Bu,Me}Cr(O)(OPh),⁷ indeed, part of our motivation for this study was the expectation that a Cr(IV)-oxo complex would be stable.

A series of deuterium-labeling experiments suggested that the ligands of the chromium complex are not the source of the hydrogen atom. We then reasoned that the elimination of all external hydrogen atom sources—that is, any molecules with weak C–H bonds—might facilitate the detection or isolation of **2**. This strategy proved successful; to wit, the reaction of [Tp^{Bu,Me}Cr(pz'H)]BARF with PhIO in pure CH₂Cl₂ carried out on a high-vacuum line yielded a

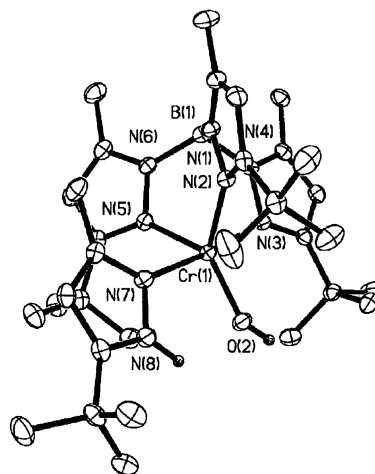
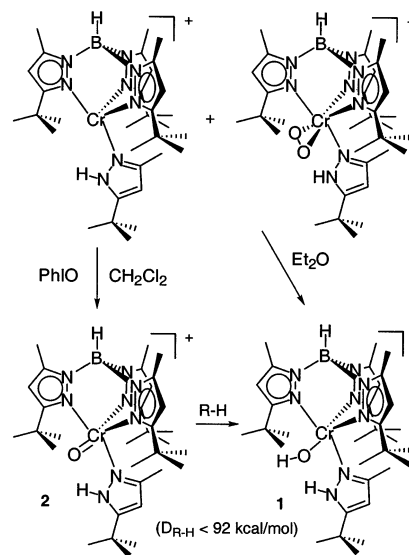


Figure 1. Molecular structure of [Tp^{Bu,Me}Cr(OH)(pz'H)]BARF (**1**); the anion has been omitted for clarity. Selected distances [Å] and angles [deg]: Cr(1)–O(2), 1.814(2); Cr(1)–N(2), 2.030(3); Cr(1)–N(3), 2.082(2); Cr(1)–N(5), 2.072(2); Cr(1)–N(7), 2.052(2); N(7)–Cr(1)–N(3), 174.62(9); O(2)–Cr(1)–N(2), 119.84(10); O(2)–Cr(1)–N(5), 140.07(11); N(2)–Cr(1)–N(5), 99.49(10); O(2)–Cr(1)–N(7), 83.68(10).

Scheme 1



green solid identified as **2**.⁸ The result of a crystal structure determination of **2** is shown in Figure 2.⁹

Similar to **1**, **2** features trigonal bipyramidal coordination of chromium (N(5) and N(7) occupy the axial positions). The most significant difference is the shorter metal–oxygen distance of **2**; at 1.602(2) Å it is consistent with a Cr=O double bond.¹⁰ This

* To whom correspondence should be addressed. E-mail: theopold@udel.edu.

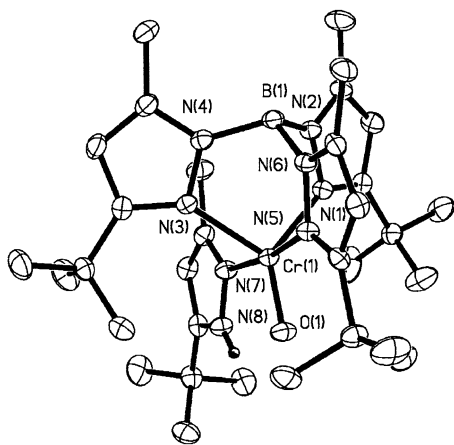


Figure 2. The molecular structure of $[\text{Tp}^{\text{tBu,Me}}\text{Cr}(\text{O})(\text{pz}'\text{H})]\text{BARF}$ (**2**); the anion has been omitted for clarity. Selected distances [Å] and angles [deg]: Cr(1)–O(1), 1.602(2); Cr(1)–N(1), 2.053(2); Cr(1)–N(3), 2.091(2); Cr(1)–N(5), 2.041(2); Cr(1)–N(7), 2.099(3); N(5)–Cr(1)–N(7), 172.03(9); O(1)–Cr(1)–N(1), 125.26(11); O(1)–Cr(1)–N(3), 133.35(11); N(1)–Cr(1)–N(3), 100.29(9); O(1)–Cr(1)–N(7), 84.56(10).

assignment is supported by the appearance of a band in the IR spectrum at 905 cm^{-1} ($\nu_{\text{Cr}=\text{O}}$), which moves to 867 cm^{-1} upon substitution with ^{18}O , and the absence of an O–H stretch. The effective magnetic moment of **2** (μ_{eff} (295 K) = $2.7(1)\ \mu_{\text{B}}$) is consistent with a formal oxidation state of Cr(IV) (d^2 , $S = 1$). The orientation of the coordinated pyrazoles raises the possibility of N–H \cdots O hydrogen-bonding interactions in both compounds.¹¹ However, while the N–O distances are in the appropriate range (**1**: N(8)–O(2), 2.58 Å; **2**: N(8)–O(1), 2.66 Å), the hydrogen atoms do not lie on the lines connecting these atoms.¹² Furthermore, the N–H stretching bands are relatively sharp and only moderately lowered in frequency (**1**: $\nu_{\text{N-H}} = 3298\text{ cm}^{-1}$; **2**: $\nu_{\text{N-H}} = 3408\text{ cm}^{-1}$ —to be compared with $\nu_{\text{N-H}} = 3435\text{ cm}^{-1}$ in $[\text{Tp}^{\text{tBu,Me}}\text{Cr}(\text{pz}'\text{H})]\text{BARF}$, which has no hydrogen bond). Considering these data, we suggest that hydrogen bonding is not a significant effect in these compounds; if at all, it is probably more important in **1**.

By itself, **2** is stable in the solid state and in methylene chloride solution, even at elevated temperatures; unlike the cobalt system it does not attack its own ligands. However, **2** abstracts hydrogen atoms from substrates of modest R–H bond strength. Thus, addition of stoichiometric amounts of 1,4-cyclohexadiene ($D_{\text{C-H}} = 73\text{ kcal/mol}$)¹³ or 9,10-dihydroanthracene ($D_{\text{C-H}} = 75.3\text{ kcal/mol}$) to CD_2Cl_2 solutions of **2** rapidly produced **1** and benzene (quantitative yield by ^1H NMR) or anthracene, respectively. Reactions with excess NEt_3 ($D_{\text{C-H}} = 90.7\text{ kcal/mol}$) or toluene ($D_{\text{C-H}} = 88\text{ kcal/mol}$) also produced **1**, albeit more slowly. Finally, dissolution of **2** in Et_2O ($D_{\text{C-H}} = 91.7\text{ kcal/mol}$) or THF ($D_{\text{C-H}} = 92\text{ kcal/mol}$) also effected its transformation into **1**. The use of THF- d_8 led to the appearance of both $\nu_{\text{O-D}}$ (2706 cm^{-1}) and $\nu_{\text{N-D}}$ (2474 cm^{-1}) in the IR spectrum of **1-d**₁. At $75\text{ }^\circ\text{C}$ $k_{\text{H}}/k_{\text{D}}$ was 10(1) for the reaction

with toluene. Collectively, these observations explain why the preparation of **2** succeeds only after the scrupulous elimination of all ready sources of hydrogen atoms.

We have demonstrated that metal complexes can transform O_2 into well-defined metal–oxo species capable of abstracting hydrogen atoms from ordinary organic compounds. A better understanding of the various factors involved (e.g., metal, oxidation state, coligands, coordination geometry, etc.) will aid the design of oxidation catalysts utilizing O_2 as the terminal oxidant.

Acknowledgment. This research was supported by a grant from the U.S. Department of Energy (ER14273).

Supporting Information Available: Characterization (PDF) and X-ray crystallographic files (in CIF format) for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Lippard, S. J.; Berg, J. M. *Principles of Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994. (b) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. (c) Mayer, J. M. *Acc. Chem. Res.* **1998**, *31*, 441. (d) Bakac, A. *J. Am. Chem. Soc.* **2002**, *124*, 9136.
- (2) (a) Egan, J. W., Jr.; Haggerty, B. S.; Rheingold, A. L.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1990**, *112*, 2445. (b) Reinaud, O. M.; Theopold, K. H. *J. Am. Chem. Soc.* **1994**, *116*, 6979. (c) Theopold, K. H.; Reinaud, O. M.; Doren, D.; Konecny, R. In *3rd World Congress on Oxidation Catalysis*; Grasselli, R. K., Oyama, S. T., Gaffney, A. M., Lyons, J. E., Eds.; Elsevier: Amsterdam, 1997; p 1081. (d) Thyagarajan, S.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *Chem. Commun.* **2001**, 2198. (e) Hikichi, S.; Komatsuzaki, H.; Akita, M.; Moro-Oka, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4699. (f) Hikichi, S.; Yoshizawa, M.; Sasakura, Y.; Akita, M.; Moro-Oka, Y. *J. Am. Chem. Soc.* **1998**, *120*, 10567.
- (3) Qin, K.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 2333.
- (4) (a) Mayer, J. M. *Comments Inorg. Chem.* **1988**, *8*, 125. (b) Bakac, A.; Espenson, J. H. *Acc. Chem. Res.* **1993**, *26*, 519.
- (5) **1**, $\text{C}_{64}\text{H}_{67}\text{B}_2\text{CrF}_{24}\text{N}_8\text{O}$, MW = 1493.88, $T = 173(2)\text{ K}$, monoclinic space group $P2_1/c$, $a = 18.8242(9)\text{ \AA}$, $b = 19.6196(9)\text{ \AA}$, $c = 19.2891(9)\text{ \AA}$, $\beta = 100.0500(10)^\circ$, $V = 7014.6(6)\text{ \AA}^3$, $Z = 4$, $R_1 = 0.0609$ [$I > 2\sigma(I)$], GOF = 1.033.
- (6) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G. *J. Chem. Soc., Dalton Trans.* **1989**, S1.
- (7) Hess, A.; Hörz, M. R.; Liable-Sands, L. M.; Lindner, D. C.; Rheingold, A. L.; Theopold, K. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 166.
- (8) CH_2Cl_2 has $D_{\text{C-H}} = 100.6\text{ kcal/mol}$ and the stabilizer it contains (amylene) was removed by repeated washing with H_2SO_4 . The byproduct of the oxygen atom transfer, i.e., iodobenzene, has only aromatic C–H bonds (similar in strength to those of benzene). The reaction is carried out on a vacuum line to prevent contamination with solvents from the drybox atmosphere.
- (9) **2**, $\frac{1}{2}\text{CH}_2\text{Cl}_2$, $\text{C}_{64.5}\text{H}_{67}\text{B}_2\text{ClCrF}_{24}\text{N}_8\text{O}$, MW = 1535.33, $T = 218(2)\text{ K}$, monoclinic space group $P2_1/c$, $a = 19.115(4)\text{ \AA}$, $b = 19.652(4)\text{ \AA}$, $c = 19.334(5)\text{ \AA}$, $\beta = 100.058(5)^\circ$, $V = 7151(3)\text{ \AA}^3$, $Z = 4$, $R_1 = 0.0777$ [$I > 2\sigma(I)$], GOF = 1.083.
- (10) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988; p 163.
- (11) (a) Shirin, Z.; Hammes, B. S.; Young, V. G., Jr.; Borovik, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 1836. (b) Macbeth, C. E.; Hammes, B. S.; Young, V. G.; Borovik, A. S. *Inorg. Chem.* **2001**, *40*, 4733.
- (12) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon: Oxford, 1984; p 357.
- (13) All bond dissociation energies from *CRC Handbook of Chemistry and Physics*, 72nd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton 1991; p 9-115.

JA028382R