J|A|C|S
COMMUNICATIONS

Formation of a Cobalt(III) Imido from a Cobalt(II) Amido Complex. Evidence for Proton-Coupled Electron Transfer

Ryan E. Cowley,[†] Ranko P. Bontchev,[‡] John Sorrell,[†] Orcino Sarracino,[†] Yanhua Feng,[†]
Haobin Wang,[†] and Jeremy M. Smith*,[†]

Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, New Mexico 88003, and
Sandia National Laboratories, P.O. Box 5800, M.S. 0779, Albuquerque, New Mexico 87185

Received September 25, 2006; E-mail: jesmith@nmsu.edu

A key step in the oxidation of water to O_2 in the catalytic cycle of photosystem II is the conversion of a MnOH species to MnO. This transformation is proposed to occur through proton-coupled electron transfer (PCET)[1] from the hydroxo ligand to a nearby tyrosyl radical.[2] Examples of this transformation in well-characterized systems are rare.[3] The reverse reaction, in which a hydrogen atom is abstracted from a substrate by a highly reactive metal oxo intermediate, is more commonly observed.[4] Imido ligands, which are often considered to be surrogates for oxos, display similar reactivity. Thus, hydrogen abstraction by imidos is often observed,[5,6] but their formation by PCET from an amido complex has not been reported.[7] Here we describe the formation of a cobalt(III) imido complex from the corresponding cobalt(II) amido complex and present computational data consistent with a concerted (PCET) pathway.

The four-coordinate complex LCoCl[8] (L = phenyltris(1-*tert*-butylimidazol-2-ylidene)borato) reacts with LiNH^{t}Bu to form the dark-green, high-spin ($S = {}^3/_2$) amido complex LCoNH^{t}Bu in high yield. This rare example of a monomeric cobalt amido complex has been crystallographically characterized (Figure 1a). The asymmetric unit consists of three crystallographically independent molecules, all showing identical structural features. The Co−N bond lengths (1.886(7)−1.88(2) Å) and bent Co−N−C linkages (152.5(2)−172.4(9)°) are comparable to those of other three- and four-coordinate cobalt amido complexes.[9]

The ^{1}H NMR spectrum of the complex is consistent with the X-ray crystal structure. Seven paramagnetically shifted resonances are observed and can be assigned on the basis of integration. A weak band at 3149 cm^{-1} in the IR spectrum is assigned to the N−H stretching vibration. Although sensitive to both water and oxygen, this complex has significantly greater thermal stability than most late transition metal alkylamido complexes, remaining unchanged for days at 100 °C.

Reaction of the amido complex with the stable 2,4,6-tri(*tert*-butyl)phenoxy radical[10] results in immediate formation of the lilac cobalt(III) imido complex LCoN^{t}Bu in high yield (Scheme 1). The diamagnetic cobalt product has been characterized by X-ray crystallography (Figure 1b) and ^{1}H NMR spectroscopy, and the 2,4,6-tri(*tert*-butyl)phenol byproduct has been characterized by ^{1}H NMR spectroscopy. The X-ray crystal structure of LCoN^{t}Bu shows similar features to related complexes. In particular, the short Co(1)−N(41) bond length (1.660(3) Å) and linear Co(1)−N(41)−C(41) bond angle (179.7(3)°) are in line with other structurally characterized cobalt(III) imidos.[11] This transformation is unique in the synthesis of late metal imido complexes, which are typically prepared via nitrene capture by low valent precursors.

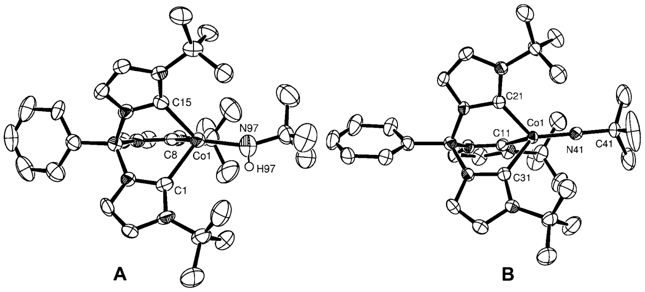
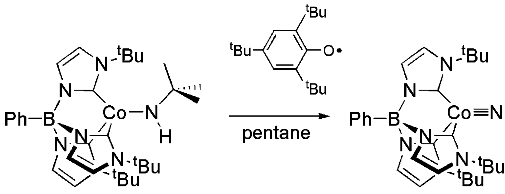
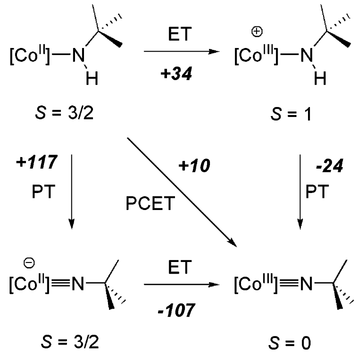


Figure 1. (a) ORTEP diagram of one of the molecules in the asymmetric unit of LCoNH^{t}Bu. Thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (deg): Co(1)−N(97) 1.886(7), Co(1)−C(1) 2.128(7), Co(1)−C(8) 2.064(7), Co(1)−C(15) 2.099(6), Co(1)−N(97)−C(28) 153.5(6), C(1)−Co(1)−C(8) 91.6(2), C(1)−Co(1)−C(15) 89.9(2), C(8)−Co(1)−C(15) 93.4(2). (b) ORTEP diagram of LCoN^{t}Bu. Thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (deg): Co(1)−N(41) 1.660(3), Co(1)−C(11) 1.988(4), Co(1)−C(21) 1.949(4), Co(1)−C(31) 1.952(4), Co(1)−N(41)−C(41) 179.7(3), C(11)−Co(1)−C(21) 90.6(2), C(11)−Co(1)−C(31) 86.8(2), C(21)−Co(1)−C(31) 87.7(2).

Scheme 1



Scheme 2. Calculated Thermodynamic Cycle in Diethyl Ether (B3LYP/6-31G*, PCM) Showing Relative Free Energies (kcal/mol)



At least three mechanisms for the formation of LCo^{III}N^{t}Bu can be proposed (Scheme 2, the corresponding organic species are not shown).[12] The cobalt(II) amido complex could react by electron transfer (ET) to form an intermediate cationic cobalt(III) amido complex, LCoNH^{t}Bu$^+$, followed by proton transfer (PT) to form the imido product, a pathway analogous to the route followed in the synthesis of (dtbpe)Ni=N(2,6-^{i}Pr$_2$C$_6$H$_3$).[13] A second possibility

---

[†] New Mexico State University.
[‡] Sandia National Laboratories.

10.1021/ja066899n CCC: $37.00

is that the cobalt(III) imido product is formed by successive PT and ET steps via an anionic cobalt(II) imido intermediate LCoN^{t}Bu$^-$. Alternatively, the reaction could occur in a concerted PCET step that avoids formation of any of the intermediates.

We have calculated the relative free energies for all species in the thermodynamic cycle using density functional theory with hybrid functional (B3LYP/6-31G*). In the cases where the spin states of the proposed intermediate cobalt complexes are not known, the energies of all possible spin states were calculated.[14] The lowest energy spin state was used to determine relative free energy barriers (Scheme 2, relative energies in kcal/mol). Diethyl ether solvent was included using the polarizable continuum model (PCM). The free energy barriers obtained using the smaller SDD basis set are comparable (within 5 kcal/mol) to those obtained with the 6-31G* basis set.

The computational results are consistent with a concerted mechanism. The pathway for PCET is lower than that for the alternative stepwise mechanisms that involve initial electron or proton transfer. We have also found that the free energy differences are similar to the electronic energy differences, and thus entropic contributions will not alter our conclusion.

Our experimental observations are consistent with the calculations. Thus, we have been unable to access the high-energy complex LCoN^{t}Bu$^-$ by deprotonation of LCoNH^{t}Bu. No reaction is observed with LDA, while in the case of MeLi, metathesis occurs to yield the previously characterized complex LCoMe.[8] Furthermore, no reduction wave was observed in the cyclic voltammogram of LCoN^{t}Bu. Likewise, initial electron transfer from LCoNH^{t}Bu to the 2,4,6-tri(*tert*-butyl)phenoxy radical was found to be thermodynamically uphill.

The relative free energies calculated for LCoNH^{t}Bu and LCoN^{t}Bu have also allowed us to estimate the gas-phase N−H BDE (enthalpy) of LCoNH^{t}Bu to be 75 kcal/mol. This is consistent with the spontaneous reaction observed with the 2,4,6-tri(*tert*-butyl)phenoxy radical (O−H BDE of 2,4,6-tri(*tert*-butyl)phenol is 81.2 kcal/mol).[15] However, we have been unable to experimentally determine a lower limit for the N−H BDE. Even substrates with weak bonds (e.g., TEMPO−H, O−H BDE = 69.7 kcal/mol),[16] do not react with LCoN^{t}Bu. This may be due to a kinetic barrier resulting from the bulkiness of the ligands, and it is thus notable that TEMPO does not react with LCoNH^{t}Bu.

In summary, we have found that a cobalt(III) imido can be prepared from the corresponding cobalt(II) amido complex. A computational investigation of the relative free energies for stepwise and concerted mechanisms is consistent with the concerted pathway involving PCET. Further studies are underway to kinetically investigate the mechanism of this transformation and extend this approach to other metals and metal−ligand multiple bonds.

Acknowledgment. This research was supported by the ACS-PRF, NMSU, and NSF CAREER (Grant CHE 0348956 to H.W.). O.S. acknowledges summer support from NIH-BRIDGES (Grant R25 GM048998). The Bruker X8 X-ray diffractometer was purchased via an NSF CRIF:MU award to the University of New Mexico, Grant CHE-0443580. We thank Eileen Duesler for the X-ray data collection and Cindy Zoski for assistance with CV measurements.

Supporting Information Available: Full synthetic, characterization, X-ray structural and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) PCET is defined as the concerted transfer of an electron and a proton. See: Mayer, J. M. *Annu. Rev. Phys. Chem.* **2004**, *55*, 363.

(2) Recent reviews: (a) Carrell, T. G.; Tyryshkin, A. M.; Dismukes, G. C. *J. Biol. Inorg. Chem.* **2002**, *7*, 2. (b) Mukhopadhyay, S.; Mandal, S. K.; Bhaduri, S.; Armstrong, W. H. *Chem. Rev.* **2004**, *104*, 3981. (c) Vrettos, J. S.; Brudvig, G. W. Oxygen Evolution. In *Comprehensive Coordination Chemistry II*, McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Oxford, 2004; pp 507−547. (d) Messinger, J. *Phys. Chem. Chem. Phys.* **2004**, *6*, 4764.

(3) Conproportionation of aqua and oxo ligands by PCET: (a) Binstead, R. A.; Stultz, L. K.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 546. (b) Nemes, A.; Bakac, A. *Inorg. Chem.* **2001**, *40*, 2720. (c) Jensen, K. B.; McKenzie, C. J.; Pedersen, J. Z. *Inorg. Chem.* **2001**, *40*, 5066.

(4) For example, in terminal iron oxo complexes: (a) Shan, X.; Que, L. *J. Inorg. Biochem.* **2006**, *100*, 421. (b) MacBeth, C. E.; Golombek, A. P.; Young, V. G.; Yang, C.; Kuczera, K.; Hendrich, M. P.; Borovik, A. S. *Science* **2000**, *289*, 938. (c) MacBeth, C. E.; Gupta, R.; Mitchell-Koch, K. R.; Young, V. G.; Lushington, G. H.; Thompson, W. H.; Hendrich, M. P.; Borovik, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 2556. (d) Pestovsky, O.; Bakac, A. *J. Am. Chem. Soc.* **2004**, *126*, 13757. (e) Kaizer, J.; Klinker, E. J.; Oh, N. Y.; Rohde, J.-U.; Song, W. J.; Stubna, A.; Kim, J.; Münck, E.; Nam, W.; Que, L. *J. Am. Chem. Soc.* **2004**, *126*, 472. (f) Oh, N. Y.; Suh, Y.; Park, M. J.; Seo, M. S.; Kim, J.; Nam, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 4235.

(5) (a) Jensen, M. P.; Mehn, M. P.; Que, L. *Angew. Chem., Int. Ed.* **2003**, *42*, 4357. (b) Kogut, E.; Wiencko, H. L.; Zhang, L.; Cordeau, D. E.; Warren, T. H. *J. Am. Chem. Soc.* **2005**, *127*, 11248. (c) Lucas, R. L.; Powell, D. R.; Borovik, A. S. *J. Am. Chem. Soc.* **2005**, *127*, 11596. (d) Eckert, N. A.; Vaddadi, S.; Stoian, S.; Lachicotte, R. J.; Cundari, T. R.; Holland, P. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 6868.

(6) (a) Thyagarajan, S.; Shay, D. T.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **2003**, *125*, 4440. (b) Shay, D. T.; Yap, G. P. A.; Zakharov, L. N.; Rheingold, A. L.; Theopold, K. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 1508.

(7) Formation of [Os^{V}]=N−NR$_2$ from [Os^{IV}]−NH−NR$_2$ by PCET: (a) Huynh, M. H. V.; Meyer, T. J.; White, P. S. *J. Am. Chem. Soc.* **1999**, *121*, 4530. (b) Huynh, M. H. V.; Meyer, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 13138.

(8) Cowley, R. E.; Bontchev, R. P.; Duesler, E. N.; Smith, J. M. *Inorg. Chem.* **2006**, *45*, 9771.

(9) (a) Murray, B. D.; Power, P. P. *Inorg. Chem.* **1984**, *23*, 4584. (b) Putzer, M. A.; Neumüller, B.; Dehnicke, K.; Magull, J. *Chem. Ber.* **1996**, *129*, 715. (c) Panda, A.; Stender, M.; Wright, R. J.; Olmstead, M. M.; Klavins, P.; Power, P. P. *Inorg. Chem.* **2002**, *41*, 3909. (d) Panda, A.; Stender, M.; Olmstead, M. M.; Klavins, P.; Power, P. P. *Polyhedron* **2003**, *22*, 67.

(10) Altwicker, E. R. *Chem. Rev.* **1967**, *67*, 475.

(11) Other cobalt(III) imidos: (a) Jenkins, D. M.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2002**, 11238. (b) Dai, X.; Kapoor, P.; Warren, T. H. *J. Am. Chem. Soc.* **2004**, *126*, 4798. (c) Hu, X.; Meyer, K. *J. Am. Chem. Soc.* **2004**, *126*, 16322. (d) Mehn, M. P.; Brown, S. D.; Jenkins, D. M.; Peters, J. C.; Que, L. *Inorg. Chem.* **2006**, *45*, 7417.

(12) (a) Mayer, J. M.; Rhile, I. J.; Larsen, F. B.; Mader, E. A.; Markle, T. F.; DiPasquale, A. G. *Photosynth. Res.* **2006**, *87*, 3. (b) Roth, J. P.; Lovell, S.; Mayer, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 5486. (c) Lebeau, E. L.; Binstead, R. A.; Meyer, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 10535. (d) Soper, J. D.; Mayer, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 12217.

(13) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2001**, *123*, 4623.

(14) Alternate spin states were found to be within 12 kcal/mol of the lowest energy spin state (see Supporting Information for details).

(15) Lucarini, M.; Pedrielli, P.; Pedulli, G. F.; Cabiddu, S.; Fattuoni, C. *J. Org. Chem.* **1996**, *61*, 9259.

(16) (a) Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X. *J. Am. Chem. Soc.* **1991**, *113*, 9790. (b) Bordwell, F. G.; Liu, W.-Z. *J. Am. Chem. Soc.* **1996**, *118*, 10819.

JA066899N