Dioxygen Activation

DOI: 10.1002/anie.201105266

Directing Protons to the Dioxygen Ligand of a Ruthenium(II) Complex with Pendent Amines in the Second Coordination Sphere**

*Tristan A. Tronic, Mary Rakowski DuBois, Werner Kaminsky, Michael K. Coggins, Tianbiao Liu, and James M. Mayer**

The activation and reduction of dioxygen (O_2) by transition-metal centers are key to a variety of biochemical and industrial processes.[1,2] Efficient reduction of dioxygen to water is also important in the operation of fuel cells.[3] These processes are typically proton-coupled electron transfer (PCET) reactions, requiring the coordinated movement of multiple protons and electrons.[4] In biological systems, it is known that initial dioxygen bonding is facilitated by hydrogen bonding and proton delivery.[5] A few recent synthetic transition-metal catalysts for oxygen reduction have utilized directed proton delivery from the metal's second coordination sphere.[6] Nocera and co-workers have pioneered using a single pendent carboxylic acid group to improve O_2 reduction catalysts by cobalt porphyrin[6a] or corrole.[6b] Yang et al. found a stronger acceleration on including non-coordinating amines as "proton relays" in nickel(II) bis-diphosphine O_2 reduction catalysis.[6c] The origins of the catalytic accelerations are not well established, however, because there are few well characterized catalytic intermediates that show the interaction of a proton relay with a dioxygen intermediate. Reported here are ruthenium–O_2 complexes with protonated and deprotonated amine proton relays, showing that the relay positions protons to form a hydrogen bond with the bound O_2.

$[Cp^*Ru(phosphine)_2]^+$ complexes form stable η^2-O_2 species with a variety of phosphine ligands ($Cp^* = \eta^5$-C_5Me_5).[7] This study used a 1,5-diaza-3,7-diphosphacyclooctane ligand with *tert*-butyl substituents on the phosphines and benzyl groups on the amines (P_2N_2),[8] similar to those used by Yang et al.[6c] Adding this ligand to $[Cp^*RuCl]_4$ yielded $[Cp^*Ru(P_2N_2)Cl]$ (Figure 1). An X-ray crystal structure and the ^1H and $^{31}P\{^1H\}$ NMR spectra confirm the structure shown (see Supporting Information). The chloride complex was converted to the η^2-dioxygen compounds $[Cp^*Ru(P_2N_2)(O_2)][X]$ ($X = PF_6^-$, BPh_4^-) by chloride abstraction with $TlPF_6$ or $NaBPh_4$ in air-saturated acetone or ethanol, respectively. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the PF_6^- and BPh_4^- salts in CD_2Cl_2 are identical, except for those peaks assigned to the anion, and are representative of this class of compounds.

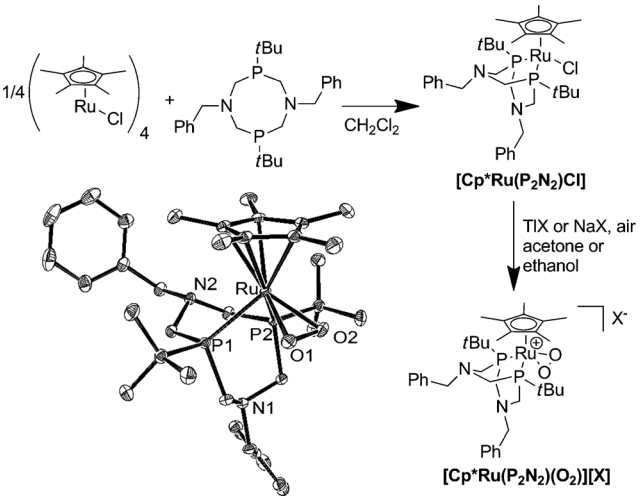


Figure 1. Synthesis of $[Cp^*Ru(P_2N_2)(O_2)][X]$ and ORTEP diagram of the cation in $[Cp^*Ru(P_2N_2)(O_2)][BPh_4]$. Thermal ellipsoids are shown at 50% probability. For clarity, hydrogen atoms have been omitted.

The X-ray crystal structure of $[Cp^*Ru(P_2N_2)(O_2)][BPh_4]$ (Figure 1) confirms the assignment. The O_2 ligand is bound essentially symmetrically η^2 to the Ru center, with Ru–O bond lengths of 2.019(1) and 2.023(1) Å. The O–O bond length of 1.401(1) Å is within the range of ca. 1.36–1.40 Å observed for other $[Cp^*Ru(phosphine)_2(O_2)]^+$ complexes,[7] and is in between the O–O distances in superoxide (KO_2, 1.28 Å)[9] and hydrogen peroxide (1.46 Å).[10] IR spectra show $\nu_{O\text{-}O} = 935\ cm^{-1}$ ($\nu_{^{18}O-^{18}O} = 880\ cm^{-1}$), consistent with an η^2-O_2 complex with this O–O bond length.[11] This complex thus could be formally described as a Ru^{IV}–peroxo complex.

$[Cp^*Ru(P_2N_2)(O_2)]^+$ and $[Cp^*Ru(P_2N_2)Cl]$ have similar ^1H and $^{31}P\{^1H\}$ NMR spectra, suggesting that the changes in electronic structure on replacing Cl^- by O_2 are not very extensive. The Cp* and *tert*-butyl resonances are slightly more downfield in the O_2 complex, by ca. 0.1 ppm, and the ^{31}P resonance is 10.6 ppm upfield. The $[Cp^*Ru(P_2N_2)(O_2)]^+$ salts are stable under vacuum and CH_2Cl_2 solutions are stable to sparging with N_2 or freeze–pump–thawing, indicating that the binding of O_2 is not reversible. The O_2 and chloride structures

[*] T. A. Tronic, Dr. W. Kaminsky, M. K. Coggins, Prof. J. M. Mayer
Department of Chemistry, University of Washington
Box 351700, Seattle, WA 98195 (USA)
E-mail: mayer@chem.washington.edu
Dr. M. Rakowski DuBois, Dr. T. Liu
Chemical and Materials Sciences Division
Pacific Northwest National Lab, Richland, WA 99352 (USA)

[**] This work is supported as part of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under FWP 56073. We thank Dr. Rajan Paranji for NMR assistance and Dr. Jenny Yang for ^{15}N-labeled P_2N_2 ligand. M.R.D. and T.L. were supported by the Division of Chemical Sciences, Biosciences and Geosciences, Office of Basic Energy Sciences, Office of Science of the U.S. Department of Energy. Pacific Northwest National Lab is operated by Battelle for the U.S. Department of Energy.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201105266.

both have the P_2N_2 ligand bound to the metal center only through the phosphorus atoms. As found in P_2N_2 complexes with other metals, the ligand structure deters the amines from chelating the metal center, as this would form strained four-membered rings.[12] The uncoordinated amines are therefore potentially able to act as second-coordination sphere proton relays, although the chair conformation of the proximal side of the P_2N_2 ligand orients N1 away from the O_2 ligand. The other amine nitrogen, N2, is on the opposite side of the ruthenium center and cannot interact with the O_2 ligand.

Treatment of $[Cp^*Ru(P_2N_2)Cl]$ with excess $LiPF_6$ and tosylic acid in aerobic methanol yielded yellow-brown crystals. NMR spectra and an X-ray crystal structure showed these to be the protonated derivative, $[Cp^*Ru(P_2N_2H)(O_2)][PF_6]_2$ (Figure 2). In the absence of tosylic acid

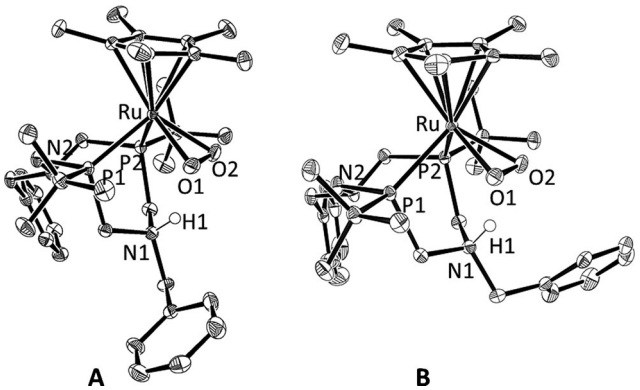
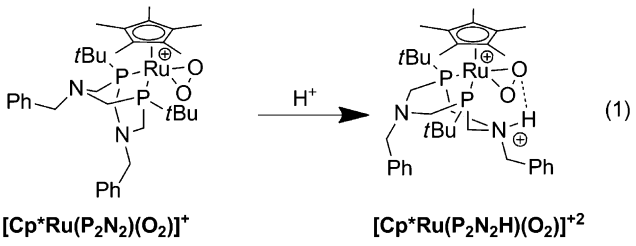


Figure 2. ORTEPs of two different structures of $[Cp^*Ru(P_2N_2H)(O_2)][PF_6]_2$: **A** ($\cdot^1/_4\,H_2O$), left, and **B** ($\cdot^1/_2$ MeOH), right, with thermal ellipsoids shown at 50% probability. For clarity, the solvent molecules, counterions, and hydrogen atoms except for the hydrogen-bonding H1, have been omitted.

the same compound is formed (determined by NMR spectroscopy), but in much lower yields. Crystals were obtained from the tosylic acid reaction which contained one water of crystallization for every four cations (structure **A**); similar crystals from a reaction without added acid were the 0.5 methanol solvate (structure **B**; Figure 2, Table 1). $[Cp^*Ru(P_2N_2H)(O_2)]^{2+}$ can also be generated in situ in CD_2Cl_2 and observed by NMR spectroscopy, using ca. 1 equiv of 2,6-dimethoxypyridine·HPF_6 [Eq. (1)].

Table 1: Relevant distances [Å] from X-ray crystal structures of $[Cp^*Ru(P_2N_2)(O_2)][BPh_4]$ and $[Cp^*Ru(P_2N_2H)(O_2)][PF_6]_2$ forms **A** and **B**.

Bond	$[Cp^*Ru(P_2N_2)(O_2)][BPh_4]$	$[Cp^*Ru(P_2N_2H)(O_2)][PF_6]_2$	
		Form **A**	Form **B**
Ru–O1	2.0229(7)	2.0393(14)	2.0260(11)
Ru–O2	2.0190(7)	2.0362(14)	2.0350(11)
O1–O2	1.4009(11)	1.405(2)	1.4161(17)
N1···O1	3.959(1)	2.846(2)	2.905(2)
N1···O2	3.978(1)	2.934(2)	2.746(2)



(1)

Structures **A** and **B**, and the NMR spectra, show that this compound has a protonated amine group. There are two PF_6^- ions per Ru center, indicating that the metal complex has a 2+ charge consistent with a protonated species. The two structures have somewhat different metrical parameters, apparently because the methanol or water molecules of crystallization are involved in different hydrogen bonding networks with the PF_6^- ions. In neither structure is the solvent interacting with the protonated or unprotonated amines, or with the O_2 ligand. In both structures, the conformation of the proximal amine is inverted relative to the structures of $[Cp^*Ru(P_2N_2)Cl]$ and $[Cp^*Ru(P_2N_2)(O_2)][BPh_4]$, bringing N1 into close proximity with the O_2 ligand. The shorter of the N···O distances in each structure, 2.846(2) Å in **A** and 2.746(2) Å in **B** (Table 1), are indicative of substantial hydrogen-bonding interactions.[13] The protonated nitrogen is somewhat farther from the other oxygen of the O_2 ligand, 2.934(2), 2.905(2) Å in **A** and **B**, respectively (Figure 2 and Supporting Information, Figure S10). In each of these structures, the η^2 binding mode of the O_2 ligand is retained. The O–O bond is essentially unchanged in form **A** ($d_{O1\text{-}O2} = 1.405(2)$ Å, within error of $[Cp^*Ru(P_2N_2)(O_2)][BPh_4]$), but is lengthened slightly in form **B** to 1.4161(17) Å ($\Delta = 0.152(20)$ Å). The O–O bond in structure **B** is, to our knowledge, longer than in any previously reported $[Cp^*Ru(phosphine)_2O_2]^+$ complex.[7] It seems likely that the longer O–O bond in structure **B** is related to the shorter N···O hydrogen bond in that structure. Though the structural changes are slight, the perturbation of the O_2 ligand on protonation is also indicated by the 30 cm^{-1} shift in $\nu_{O\text{-}O}$ to 905 cm^{-1} ($\nu_{^{18}O-^{18}O} = 840$) cm^{-1}.

^1H NMR spectra of $[Cp^*Ru(P_2N_2H)(O_2)][PF_6]_2$ in CD_2Cl_2 show sharp resonances that are consistent with the crystal structures. Half of the benzylic CH_2 and PCH_2N resonances are shifted downfield by ca. 1 ppm relative to $[Cp^*Ru(P_2N_2)(O_2)][PF_6]$, consistent with protonation of one of the two amine nitrogens. Additionally, the downfield benzylic CH_2 is split into a doublet ($J_{HH} = 3$ Hz) due to coupling with the N*H*, while the upfield benzyl resonance is a singlet (as in the spectra of the unprotonated complexes). The $^{31}P\{^1H\}$ spectrum shows a broad resonance, rather than the sharp singlet observed for $[Cp^*Ru(P_2N_2)(O_2)][PF_6]$. Lowering the temperature to −60 °C causes decoalescence into two signals. The barrier to this process at −20 °C is ca. 10 kcal mol^{-1} (see Supporting Information). This process is not exchange between protonated and unprotonated species, as NMR spectra of $[Cp^*Ru(P_2N_2)(O_2)][PF_6]$ with less than 1 equiv of dimethoxypyridine·HPF_6 show both this broad resonance and the sharp resonance of $[Cp^*Ru(P_2N_2)(O_2)][PF_6]$. These spectra may reflect a fluxional process in which the proton-

ated amine exchanges between hydrogen bonding to O1 and O2, as suggested by the asymmetric structures in the solid state.

The location of the proton on the amine has been further confirmed by ^{1}H-^{15}N NMR spectra in CH_2Cl_2 of the ^{15}N-labeled compound. The 1-D heteronuclear single quantum coherence (HSQC) spectrum of $[Cp^*Ru(P_2{}^{15}N_2H)(O_2)][PF_6]_2$ has a single peak at 7.6 ppm and the $J_{^1H-^{15}N}$ of 76 Hz shows the presence of an N–H bond. The downfield ^1H NMR chemical shift is suggestive of a hydrogen-bonding environment.[13] The chemical shift and coupling constant are also consistent with the proton being located on one benzylamine rather than bridged between two benzylamines. Such benzylamine-bridged species have previously been determined to have chemical shifts of ca. 15 ppm and $J_{^1H-^{15}N} \approx 30$ Hz.[14]

Density functional theory (DFT) calculations were performed to further support the proposed protonated structure. Gas-phase calculations (BP86/6-31G**(SDD)) were performed with Gaussian09.[15] Optimizations of $[Cp^*Ru(P_2N_2)(O_2)]^+$ and $[Cp^*Ru(P_2N_2H)(O_2)]^{2+}$ gave structures very similar to those found in the crystal structures. In the latter, the protonated amine nitrogen N1 is calculated to form a short hydrogen bond to O1 ($d_{N1\text{-}O1} = 2.65$ Å), with a considerably longer distance to the other oxygen ($d_{N1\text{-}O2} = 3.00$ Å), as in the crystal structures. The calculated $d_{O1\text{-}O2}$ lengthens upon protonation, by 0.015 Å, consistent with the change observed crystallographically. The use of other functionals or larger basis sets gave similar geometries, and consistently showed a change in $d_{O1\text{-}O2}$ of ca. 0.015 Å (see Supporting Information), suggesting that the change in $d_{O1\text{-}O2}$, though relatively small, is due to the presence of the proton. The calculated $\nu_{^{16}O-^{16}O}$ is shifted from 976 cm^{-1} to 951 cm^{-1} with protonation, consistent with the ca. 30 cm^{-1} shift observed experimentally.

Another minimum was located with the proton bound to N2, on the opposite side of the ruthenium from the O_2 ligand. However, the energy of this species is calculated to be 23 kcal mol^{-1} above the isomer with N1 protonated. In the N2-protonated structure, and in the unprotonated O_2 structure, the N1···O distances are both long, ca. 3.1 Å. Furthermore, the calculated O–O bond in the N2-protonated form is actually 0.008 Å shorter than in the calculated structure of $[Cp^*Ru(P_2N_2)(O_2)]^+$. Additionally, the calculated $d_{O1\text{-}O2}$ in $[Cp^*Ru(P_2N_2)(O_2)]^+$ is not affected by the P_2N_2 conformation, since the same bond length is found in an alternative higher energy-minimized structure obtained by optimization starting from the ligand geometry of $[Cp^*Ru(P_2N_2H)(O_2)]^{2+}$, but without including the acidic proton. In sum, locating the proton in positions other than N1 did not lead to good agreement with the crystal structures, and therefore the DFT calculations support the structure of $[Cp^*Ru(P_2N_2H)(O_2)]^{2+}$ as N1-protonated and that this protonation lengthens the O–O bond.

The presence of the proton on the amine makes reduction of the dioxygen complex significantly more facile. A cyclic voltammogram (CV) of $[Cp^*Ru(P_2N_2)(O_2)][PF_6]$ in CH_2Cl_2 has an irreversible reduction wave with a peak at −1.47 V vs. $Cp_2Fe^{+/0}$ (Figure 3). Upon the addition of triflic acid, a new irreversible reduction wave appears, shifted by +0.67 V. An identical peak is seen in the CV of isolated $[Cp^*Ru(P_2N_2H)(O_2)][PF_6]_2$ (Figure S15). Ongoing work is examining the products of these reductions.

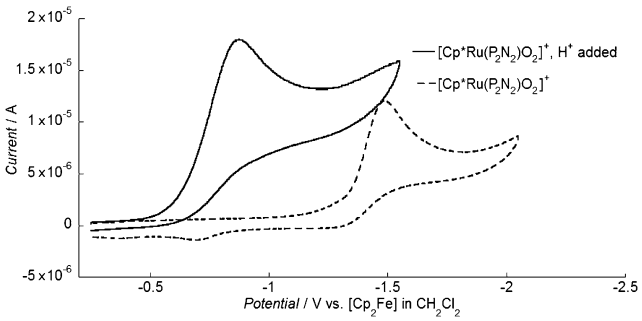


Figure 3. Cyclic voltammograms of $[Cp^*Ru(P_2N_2)(O_2)][PF_6]$ (1.2 mM) (gray, dashed line) and $[Cp^*Ru(P_2N_2)(O_2)][PF_6]$ with HOTf added (black, solid line) in CH_2Cl_2, 0.1 M $[nBu_4N][PF_6]$, scan rate 0.1 Vs^{-1}.

In summary, a ruthenium η^2-O_2 complex has been synthesized with a pendent amine in the second coordination sphere of the metal. The crystal structures, NMR and IR data indicate that the pendent amine can bind a proton, and that the resulting ammonium ion forms a hydrogen bond with the O_2 ligand, slightly lengthening the O–O bond. Experiments are underway to test how protonation affects the reactivity of this complex and how the relays affect its ability to act as a catalyst for O_2 reduction.

Received: July 27, 2011
Revised: August 30, 2011
Published online: September 26, 2011

Keywords: dioxygen ligands · hydrogen bonding · O-O activation · protonation · proton-coupled electron transfer

[1] a) V. R. I. Kaila, M. I. Verkhovsky, M. Wikström, *Chem. Rev.* **2010**, *110*, 7062–7081; b) E. I. Solomon, P. Chen, M. Metz, S.-K. Lee, A. E. Palmer, *Angew. Chem.* **2001**, *113*, 4702–4724; *Angew. Chem. Int. Ed.* **2001**, *40*, 4570–4590; c) I. G. Denisov, T. M. Makris, S. G. Sligar, I. Schlichting, *Chem. Rev.* **2005**, *105*, 2253–2278; d) M. Sono, M. P. Roach, E. D. Coulter, J. H. Dawson, *Chem. Rev.* **1996**, *96*, 2841–2888.

[2] a) A. S. Matlack, *Introduction to Green Chemistry*, Marcel Dekker, New York, **2001**; b) S. S. Stahl, *Angew. Chem.* **2004**, *116*, 3480–3501; *Angew. Chem. Int. Ed.* **2004**, *43*, 3400–3420; c) S. S. Stahl, *Science* **2005**, *309*, 1824–1826.

[3] M. Winter, R. J. Brodd, *Chem. Rev.* **2004**, *104*, 4245–4270.

[4] a) J. J. Warren, T. A. Tronic, J. M. Mayer, *Chem. Rev.* **2010**, *110*, 6961–7001; b) J.-M. Savéant, *Chem. Rev.* **2008**, *108*, 2348–2378.

[5] a) J. N. Rodriguez-Lopez, A. T. Smith, R. N. F. Thorneley, *J. Biol. Chem.* **1997**, *272*, 389–395; b) D. A. Proshlyakov, M. A. Pressler, G. T. Babcock, *Proc. Natl. Acad. Sci. USA* **1998**, *95*, 8020–8025; c) D. Hamdane, H. Zhang, P. Hollenberg, *Photosynth. Res.* **2008**, *98*, 657–666; d) W. J. Song, M. S. McCormick, R. K. Behan, M. H. Sazinsky, W. Jiang, J. Lin, C. Krebs, S. J. Lippard, *J. Am. Chem. Soc.* **2010**, *132*, 13582–13585.

[6] a) R. McGuire, Jr., D. K. Dogutan, T. S. Teets, J. Suntivich, Y. Shao-Horn, D. G. Nocera, *Chem. Sci.* **2010**, *1*, 411–414; b) D. K. Dogutan, S. A. Stoian, R. McGuire, M. Schwalbe, T. S. Teets, D. G. Nocera, *J. Am. Chem. Soc.* **2010**, *133*, 131–140; c) J. Y.

Yang, R. M. Bullock, W. G. Dougherty, W. S. Kassel, B. Twamley, D. L. DuBois, M. Rakowski DuBois, *Dalton Trans.* **2010**, *39*, 3001 – 3010; d) R. L. Shook, S. M. Peterson, J. Greaves, C. Moore, A. L. Rheingold, A. S. Borovik, *J. Am. Chem. Soc.* **2011**, *133*, 5810 – 5817.

[7] a) K. Kirchner, K. Mauthner, K. Mereiter, R. Schmid, *J. Chem. Soc. Chem. Commun.* **1993**, 892; b) K. Mauthner, K. Mereiter, R. Schmid, K. Kirchner, *Inorg. Chim. Acta* **1995**, *236*, 95 – 100; c) M. Sato, M. Asai, *J. Organomet. Chem.* **1996**, *508*, 121 – 127; d) E. Lindner, M. Haustein, R. Fawzi, M. Steimann, P. Wegner, *Organometallics* **1994**, *13*, 5021 – 5029; e) G. Jia, W. S. Ng, H. S. Chu, W.-T. Wong, N.-T. Yu, I. D. Williams, *Organometallics* **1999**, *18*, 3597 – 3602; f) I. de Los Ríos, M. Jiménez Tenorio, J. Padilla, M. C. Puerta, P. Valerga, *Organometallics* **1996**, *15*, 4565 – 4574.

[8] E. S. Wiedner, J. Y. Yang, W. G. Dougherty, W. S. Kassel, R. M. Bullock, M. Rakowski DuBois, D. L. DuBois, *Organometallics* **2010**, *29*, 5390 – 5401.

[9] J. S. Valentine, *Chem. Rev.* **1973**, *73*, 235 – 245.

[10] J. M. Savariault, M. S. Lehmann, *J. Am. Chem. Soc.* **1980**, *102*, 1298 – 1303.

[11] C. J. Cramer, W. B. Tolman, K. H. Theopold, A. L. Rheingold, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 3635 – 3640.

[12] M. Rakowski DuBois, D. L. DuBois, *Chem. Soc. Rev.* **2009**, *38*, 62 – 72.

[13] a) T. Steiner, *Angew. Chem.* **2002**, *114*, 50 – 80; *Angew. Chem. Int. Ed.* **2002**, *41*, 48 – 76; b) G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, Oxford, **1997**.

[14] A. D. Wilson, R. K. Shoemaker, A. Miedaner, J. T. Muckerman, D. L. DuBois, M. Rakowski DuBois, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 6951 – 6956.

[15] R. B. Gaussian 09, M. J. Frisch, et al. See Supporting Information.

