

## Two-Step Binding of O<sub>2</sub> to a Vanadium(III) Trisanilide Complex To Form a Non-Vanadyl Vanadium(V) Peroxo Complex

Anthony F. Cozzolino,<sup>†</sup> Daniel Tofan,<sup>†</sup> Christopher C. Cummins,<sup>\*,†</sup> Manuel Temprado,<sup>\*,‡</sup> Taryn D. Palluccio,<sup>§</sup> Elena V. Rybak-Akimova,<sup>\*,§</sup> Subhojit Majumdar,<sup>||</sup> Xiaochen Cai,<sup>||</sup> Burjor Captain,<sup>||</sup> and Carl D. Hoff<sup>\*,||</sup>

<sup>†</sup>Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States

<sup>‡</sup>Department of Physical Chemistry, Universidad de Alcalá, Ctra. Madrid-Barcelona Km. 33,600, Madrid 28871, Spain

<sup>§</sup>Department of Chemistry, Tufts University, 62 Talbot Avenue, Medford, Massachusetts 02155, United States

<sup>||</sup>Department of Chemistry, University of Miami, 1301 Memorial Drive, Coral Gables, Florida 33021, United States

### S Supporting Information

**ABSTRACT:** Treatment of V(N[<sup>t</sup>Bu]Ar)<sub>3</sub> (**1**) (Ar = 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) with O<sub>2</sub> was shown by stopped-flow kinetic studies to result in the rapid formation of (η<sup>1</sup>-O<sub>2</sub>)V(N[<sup>t</sup>Bu]Ar)<sub>3</sub> (**2**) (ΔH<sup>‡</sup> = 3.3 ± 0.2 kcal/mol and ΔS<sup>‡</sup> = -22 ± 1 cal mol<sup>-1</sup> K<sup>-1</sup>), which subsequently isomerizes to (η<sup>2</sup>-O<sub>2</sub>)V(N[<sup>t</sup>Bu]Ar)<sub>3</sub> (**3**) (ΔH<sup>‡</sup> = 10.3 ± 0.9 kcal/mol and ΔS<sup>‡</sup> = -6 ± 4 cal mol<sup>-1</sup> K<sup>-1</sup>). The enthalpy of binding of O<sub>2</sub> to form **3** is -75.0 ± 2.0 kcal/mol, as measured by solution calorimetry. The reaction of **3** and **1** to form 2 equiv of O≡V(N[<sup>t</sup>Bu]Ar)<sub>3</sub> (**4**) occurs by initial isomerization of **3** to **2**. The results of computational studies of this rearrangement (ΔH = 4.2 kcal/mol; ΔH<sup>‡</sup> = 16 kcal/mol) are in accord with experimental data (ΔH = 4 ± 3 kcal/mol; ΔH<sup>‡</sup> = 14 ± 3 kcal/mol). With the aim of suppressing the formation of **4**, the reaction of O<sub>2</sub> with **1** in the presence of <sup>t</sup>BuCN was studied. At -45 °C, the principal products of this reaction are **3** and <sup>t</sup>BuC(=O)N≡V(N[<sup>t</sup>Bu]Ar)<sub>3</sub> (**5**), in which the bound nitrile has been oxidized. Crystal structures of **3** and **5** are reported.

Activation of dioxygen at a single transition-metal center can yield either end-bound (η<sup>1</sup>) or side-bound (η<sup>2</sup>) complexes.<sup>1</sup> It is generally held that the η<sup>1</sup> binding motif is more reactive than the η<sup>2</sup> motif.<sup>2</sup> The formation of side-bound O<sub>2</sub> complexes can proceed by initial end-on binding followed by isomerization or possibly by concerted binding of O<sub>2</sub> to form the side-bound product. In spite of the fact that the two-step activation of O<sub>2</sub> to form a side-bound adduct is logical, limited evidence for this pathway exists. Cases where both forms of binding can be observed are rare, and there are few quantitative kinetic studies in which the rates of binding and interconversion have been directly measured. Kinetic data obtained for the treatment of four- and five-coordinate iridium(I) complexes with oxygen are in keeping with initial end-on binding followed by rapid rearrangement upon dissociation of a ligand,<sup>3</sup> but since ligand dissociation is a prerequisite for η<sup>2</sup> coordination, that result is not reflective of systems having an open coordination site, where η<sup>2</sup> binding could in principle occur directly. Treatment of a Cu<sup>I</sup> complex

with O<sub>2</sub> leads to a side-bound O<sub>2</sub> complex that density functional theory (DFT) calculations indicate is formed by initial end-on binding followed by a low-barrier isomerization to give the final side-bound product.<sup>4</sup> It has recently been shown that increasing the steric constraints with bulky ligands yields bis-superoxo binding of O<sub>2</sub> in the complex (η<sup>1</sup>-O<sub>2</sub>)<sub>2</sub>Pd(IPr)<sub>2</sub> [IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene]<sup>5</sup> as opposed to single peroxo binding in (η<sup>2</sup>-O<sub>2</sub>)Pd(IMes)<sub>2</sub> [IMes = *N,N'*-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene].<sup>6</sup>

Vanadium peroxo complexes are important as both natural<sup>7</sup> and industrial<sup>8</sup> oxidation catalysts. Vanadium peroxides are typically formed from V<sup>IV</sup> or V<sup>V</sup> by reaction with hydrogen peroxide or alkyl hydroperoxides;<sup>9</sup> there are limited examples where O<sub>2</sub> is the oxidant.<sup>10</sup> In fact, there are only a limited number of cases in which structurally characterized early transition-metal peroxo complexes have been prepared directly by reaction with O<sub>2</sub>.<sup>11</sup> In the case of V<sup>III</sup> complexes, oxidation by O<sub>2</sub> typically produces a V<sup>V</sup> oxo species resulting from a bimetallic, four-electron reduction of O<sub>2</sub>.<sup>12</sup> In this work, we report studies of O<sub>2</sub> binding to the sterically crowded early transition-metal complex V(N[<sup>t</sup>Bu]Ar)<sub>3</sub> (**1**) (Ar = 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), which proceeds through an η<sup>1</sup>-peroxo complex.

The reactions of **1** with a variety of oxygen atom transfer (OAT) reagents to form cleanly the vanadium oxo complex O≡V(N[<sup>t</sup>Bu]Ar)<sub>3</sub> (**4**) were recently investigated.<sup>13</sup> The O≡V bond in **4** (154 ± 3 kcal/mol)<sup>13</sup> is strong enough that the reaction of V(N[<sup>t</sup>Bu]Ar)<sub>3</sub> with O<sub>2</sub> to generate an O atom is thermodynamically favorable, as shown in eq 1:



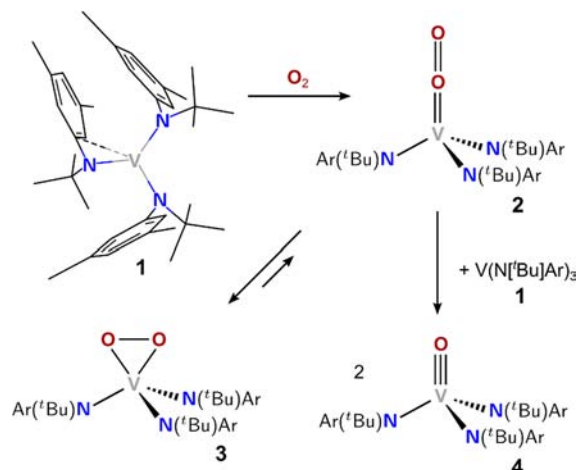
The reaction of **1** with excess O<sub>2</sub> in toluene at -78 °C irreversibly produced a forest-green-colored solution, in contrast to the red-orange color of **4**. NMR studies showed the green complex to be a diamagnetic species that slowly decomposed upon warming with minimal production of **4**. Addition of excess **1** followed by warming to room temperature

Received: September 28, 2012

Published: October 19, 2012

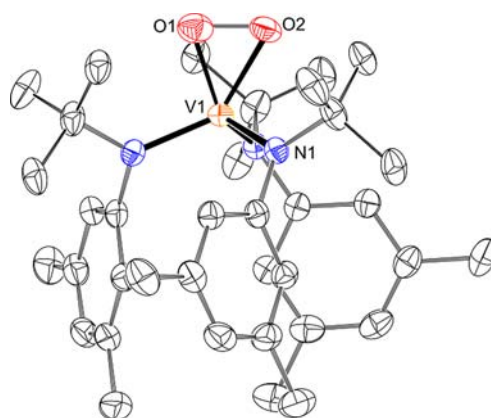
did lead to production of **4**. These observations suggested the sequence of reactions shown in Scheme 1.

Scheme 1



Initial attempts to isolate pure crystals of **3** were frustrated by contamination with **4**, which has the same unit cell parameters as **3** and readily cocrystallizes with it. Since the reaction of **3** with **1** produces **4**, it was felt that reaction of a weakly bound nitrile adduct of **1** would minimize the concentration of free **1**, resulting in cleaner formation of **3** with less production of **4** when  $O_2$  was delivered to a concentrated solution of **1**. Stopped-flow kinetic and NMR studies would later show that at temperatures below  $-30$  °C, the reaction of **3** and **1** is sufficiently slow that tempering the reactivity of **1** by this weak ligand binding is not required when  $O_2$  is present in excess. A fortuitous byproduct of the “nitrile method” was the accidental discovery of the pivaloylimido complex  $tBuC(=O)N\equiv V(N[Ar]tBu)_3$  (**5**), as discussed later.

The “nitrile method” proved to be a facile way to prepare and ultimately to isolate gram quantities of **3** at room temperature.  $^{51}V$  NMR spectroscopy showed no contamination by **4** ( $-171$  ppm) and only a peak at  $198$  ppm due to **3**. This is a very high frequency relative to those for known  $V^V$  peroxides ( $-520$  to  $-650$  ppm)<sup>14</sup> and is reflective of the unique ligand environment used to support the vanadium peroxide moiety in **3**, including the lack of a vanadyl moiety. Diffraction-quality crystals of **3** were obtained by recrystallizing **3** from pentane at  $-35$  °C. The asymmetric unit consists of one-third of a molecule, the remainder being generated by a crystallographic threefold axis (Figure 1). This necessitates the disorder of the peroxy moiety over three positions, as clearly seen in the density map [Figure S1 in the Supporting Information (SI)]. The full molecule has a five-coordinate  $V^V$  center with two of the coordination sites occupied by the two oxygen atoms of the peroxy ligand. This is the first structurally characterized example of a non-vanadyl peroxy species,<sup>15</sup> with the exception of per(peroxy)vanadium structures.<sup>16</sup> The structure exhibits unequal V–O bond distances [ $1.777(4)$  and  $1.908(4)$  Å], the average of which ( $1.843$  Å) is shorter than the average V–O<sub>peroxy</sub> distance of structurally characterized vanadium peroxy systems ( $1.878$  Å).<sup>17</sup> The oxygen atom that is farther away ( $O_2$ ) appears to engage in a weak hydrogen bond with a neighboring  $CH_{aryl-Me}$  [ $O\cdots H = 2.68$  Å,  $C(H)\cdots O = 3.36$  Å; Figure S2]<sup>18</sup> and furthermore is located trans to a V–N bond [ $141.5(1)^\circ$ ]. Thus, the V– $O_2$  bond is likely lengthened



**Figure 1.** Solid-state structure of **3** with thermal ellipsoids at 50% probability. H atoms, symmetry-related O atoms, and disordered  $tBu$  groups have been omitted for clarity. Selected distances (Å) and angles (deg): V1–N1, 1.887(1); V1–O1, 1.777(4); V1–O2, 1.908(4); O1–O2, 1.416(5); O1–V1–O2, 45.1(2).

because of the synergistic influences of the hydrogen bond and the trans anilide ligand. The O–O peroxide bond length [ $1.416(5)$  Å] is also short compared with the average O–O bond in known  $V^V(O_2)$  complexes (average  $1.430$  Å, median  $1.436$  Å).<sup>17</sup>

Stopped-flow kinetic studies gave clear evidence for a two-step binding process. All reactions were studied under pseudo-first-order conditions using excess  $O_2$ . Binding of  $O_2$  to **1** occurred within seconds at low temperatures ( $-80$  to  $-53$  °C). Upon mixing, a rapid growth in absorbance was observed across most of the spectrum ( $\lambda = 400$ – $682$  nm) with concomitant decay occurring at longer wavelengths ( $\lambda = 682$ – $800$  nm). The first process showed a linear dependence on  $[O_2]$  (Figure S12) and a low activation enthalpy ( $\Delta H^\ddagger$ ) of  $3.3 \pm 0.2$  kcal/mol, typical of  $O_2$  binding at a vacant metal site.<sup>5,19</sup> This rapid, low-barrier process was followed by a slower process characterized by an increase in absorbance at  $\lambda = 400$ – $682$  nm with concomitant decay occurring at  $\lambda = 682$ – $800$  nm (see SI). This second slower step, which was found to be independent of  $[O_2]$  (Table S3) and to have a much higher  $\Delta H^\ddagger$  and much lower activation entropy ( $\Delta S^\ddagger$ ) than the initial bimolecular reaction step ( $\Delta H^\ddagger = 10.3 \pm 0.9$  kcal/mol and  $\Delta S^\ddagger = -6 \pm 4$  cal mol<sup>-1</sup> K<sup>-1</sup>; Figure S14), is assigned to the rearrangement of **2** to **3** (Scheme 1). Solution calorimetric studies of the reaction of **1** with  $O_2$  to form **3** ( $10$  °C in heptane) yielded  $\Delta H = -75.0 \pm 2.0$  kcal/mol.

Binding of  $O_2$  to **1** was investigated computationally, and DFT geometry optimizations of the  $\eta^1-O_2$  and  $\eta^2-O_2$  complexes were carried out for both the singlet and triplet spin states. The minimal-energy triplet geometry was found to be  $26.2$  kcal/mol higher than the minimal singlet geometry. For the singlet manifold, two stable structures were computed, corresponding to the  $\eta^1$  complex **2** and the  $\eta^2$  complex **3**. A small energy difference of only  $4.2$  kcal/mol was found for the two isomers, favoring  $\eta^2$  binding. The DFT-minimized structure of **3** contains a more symmetrical peroxy ligand than found experimentally. The computed V–O distances are  $1.830$  and  $1.851$  Å, and the O–O distance is  $1.471$  Å. Minimization of **3** while constraining it to have the crystallographic V–O and O–O metrics gave an energy that is only  $2.4$  kcal/mol higher, an increase for which the formation of the weak hydrogen bond ( $<4$  kcal/mol) compensates.<sup>18a</sup>

The computed metrical parameters and electronic structure of **2** are consistent with its formulation as a  $V^V$  peroxy as opposed to a  $V^{IV}$  superoxo species. The DFT-calculated  $\eta^1$ - $O_2$  complex has a V–O distance of 1.676 Å, an O–O distance of 1.307 Å, and a V–O–O bond angle of 179.3°. The Mayer bond order<sup>20</sup> of the O–O bond decreases upon isomerization, going from 0.98 in **2** to 0.82 in **3**, consistent with a more activated, albeit less accessible,  $O_2$  in the side-bound adduct. The end-bound complex has a Mayer bond order of 1.13 for the V–O bond, which is an increase in multiple-bond character with respect to the V–O bonds in **3** (ave 0.93 Å), consistent with the short V–O bond length. In fact, the main contributing resonance structure according to natural resonance theory analysis<sup>21</sup> contains a V–O double bond and an O–O single bond; the main contributing resonance structure for **3** contains two V–O single bonds and an O–O single bond. The potential energy surface for the isomerization of **2** to **3** was mapped by varying the V–O–O bond angle from 180 to 67° (Figure 2). A

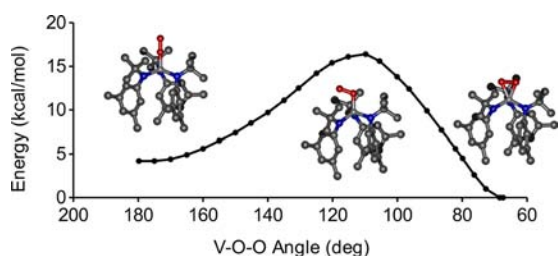


Figure 2. DFT-calculated potential energy surface for isomerization of **2** to **3**.

transition state ( $[2]^\ddagger$ ) was located at a V–O–O angle of 109.8°, providing an activation energy of 12.2 kcal/mol for the  $\eta^1$  to  $\eta^2$  process, which is in good agreement with experiment. The isoelectronic chromium nitrosyl complexes, which are known to be N-bound, have been previously isolated and were readily deoxygenated by (THF)V(Mes)<sub>3</sub> to give the terminal  $Cr^{VI}$  nitrido species.<sup>22</sup> If the analogous  $\eta^1$ - $O_2$  species exists in equilibrium with peroxy **3**, then addition of **1** could be used to deoxygenate peroxy **2** to give **2** equiv of oxo **4** (Scheme 1). Indeed, <sup>1</sup>H NMR spectroscopic kinetic studies of the reaction of **3** with **1** confirmed this, and an activation energy of  $14 \pm 3$  kcal/mol was determined for this process (Figures S22–S24). The computed  $\Delta H^\ddagger$  for conversion of **3** to **2** (16.4 kcal/mol) is in good agreement with the experimental value. Despite the fact that it is thermodynamically comparable to  $N_2O$  as an OAT reagent, the deoxygenation of peroxy **3** by vanadium(III) complex **1** is relatively slow. This is interpreted to be a result of the requisite formation of **2**, which is sterically more accessible for OAT with **1** than is **3**, as illustrated by the Fukui functions when plotted on the electron density (Figures S3–S5).<sup>23</sup>

Figure 3 shows a combined potential energy diagram for this system in which the experimental energy of  $O_2$  binding has been combined with the computed relative energies for **2** and **3** binding and interconversion; also incorporated in the diagram are the activation energies from the stopped-flow experiments and the <sup>1</sup>H NMR experiments. For reasons that are not yet understood, the overall computed  $\Delta H$  of binding of  $O_2$  to **1** to yield **3** is  $-51.2$  kcal/mol, which is in nontrivial disagreement with the experimental value of  $-75$  kcal/mol. In contrast, good agreement between theory and experiment was found for the computed  $O \equiv V$  bond strength in **4**.<sup>13</sup>

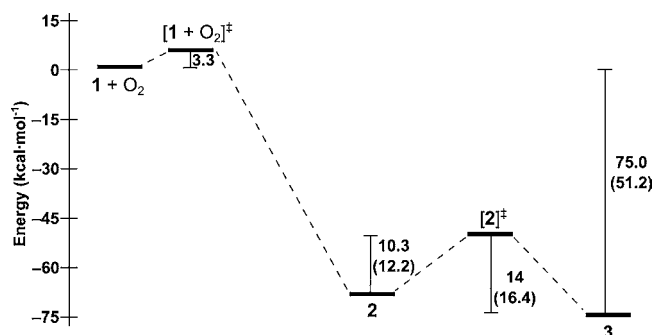


Figure 3. Experimental and DFT-calculated (in parentheses) potential energy diagram for the reaction between  $O_2$  and **1** to ultimately form **3**. Energies are given in kcal/mol.

Finally, during attempts to obtain pure **3** by addition of <sup>t</sup>BuCN to **1** followed by reaction with  $O_2$ , it was observed that at  $-45$  °C a change in color from royal purple to dark green occurred over the course of 1 h. The reaction mixture was assayed by <sup>51</sup>V NMR spectroscopy and found to contain **3** and a new product whose <sup>51</sup>V NMR signal was split into a 1:1:1 triplet (Figure 4 inset). Crystals of the new product were

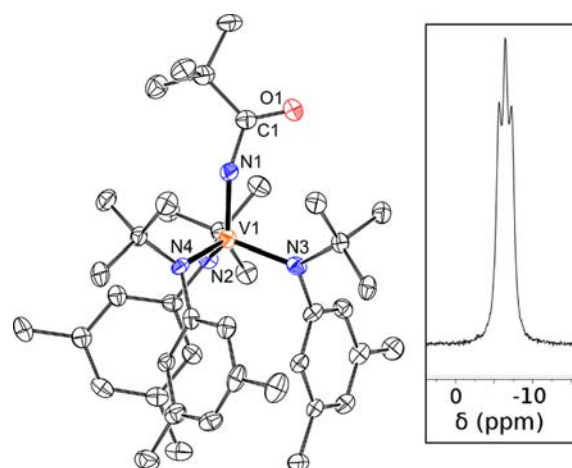


Figure 4. Solid-state structure of **5** with thermal ellipsoids at 50% probability and H atoms omitted for clarity. Selected distances (Å) and angles (deg): V1–N1, 1.695(3); V1–N2, 1.875(2); V1–N3, 1.888(2); V1–N4, 1.894(3); N1–C1, 1.390(4); C1=O1, 1.218(4); V1–N1–C1, 151.9(2); N1–C1=O1, 120.8(3); N1–C1–C11, 118.0(3). Inset: <sup>51</sup>V NMR spectrum of **5** in THF.

isolated manually and determined to be the result of oxidation of the bound nitrile to form the acylimido species **5** (Figure 4). Acylimido moieties have been prepared by the treatment of terminal metal nitrides with acylating agents.<sup>24</sup> Rarer is the direct oxidation of a metal-bound nitrile to form the acylimido.<sup>25</sup> In **5**, the spin–spin coupling is assigned to <sup>1</sup>J<sup>14</sup><sub>N–<sup>51</sup>V</sub> coupling (83 Hz). The identity of **5** was confirmed by its independent synthesis from Na[N≡V(N[<sup>t</sup>Bu]Ar)<sub>3</sub>]<sup>26</sup> and pivaloyl chloride.

Despite the industrial and biological importance of oxidation reactions mediated by metal centers,<sup>7,8</sup> the formation of early metal peroxides by the direct reaction of a low-valent and unsaturated transition-metal complex with  $O_2$  is still remarkably rare. We have isolated and structurally characterized the first non-vanadyl  $V^V$  peroxide from the controlled reaction of an unsaturated  $V^{III}$  complex with  $O_2$ . Moreover, we have observed



the  $\eta^1$ – $\eta^2$  conversion in O<sub>2</sub> binding, which is a pathway that has been proposed as a general step in  $\eta^2$ -peroxide formation from O<sub>2</sub>.<sup>1</sup> Solution calorimetric studies of the binding of O<sub>2</sub> to **1** suggest that peroxo **3** should be a potent oxidant. It is encouraging that careful tailoring of the reaction conditions led to the clean generation of peroxide **3** from O<sub>2</sub>, suggesting that similar control may be applied more generally to other low-valent and unsaturated early transition-metal complexes, leading to a class of thermodynamically potent OAT reagents.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details for synthesis, stopped-flow kinetic, and thermochemical studies; crystal structure files for **3** (CCDC 893666) and **5** (CCDC 893667); and computational details for **2**, **3**, and their interconversion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

ccummins@mit.edu; manuel.temprado@uah.es; elena.rybak-akimova@tufts.edu; c.hoff@miami.edu

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This material is based upon work supported by (a) the National Science Foundation under Grants CHE-1111357 (C.C.C.), CHE-0615743 (C.D.H.), CHE-0750140 (E.V.R.-A.), and CRIF-0639138 (E.V.R.-A.); (b) the Spanish Ministry of Science and Innovation (MICINN) CTQ2009-07120 (M.T.); (c) the Natural Sciences and Engineering Research Council of Canada postdoctoral fellowship (A.F.C.); and (d) a GAANN Fellowship (T.D.P.).

## ■ REFERENCES

- (1) Rybak-Akimova, E. V. In *Physical Inorganic Chemistry: Reactions, Processes, and Applications*; Bakac, A., Ed.; Wiley: Hoboken, NJ, 2010; pp 109–188.
- (2) Unno, M.; Chen, H.; Kusama, S.; Shaik, S.; Ikeda-Saito, M. *J. Am. Chem. Soc.* **2007**, *129*, 13394–13395.
- (3) De Waal, D. J. A.; Gerber, T. I. A.; Louw, W. J.; Van Eldik, R. *Inorg. Chem.* **1982**, *21*, 2002–2006.
- (4) Aboeella, N. W.; Kryatov, S. V.; Gherman, B. F.; Brennessel, W. W.; Young, V. G.; Sarangi, R.; Rybak-Akimova, E. V.; Hodgson, K. O.; Hedman, B.; Solomon, E. I.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **2004**, *126*, 16896–16911.
- (5) Cai, X.; Majumdar, S.; Fortman, G. C.; Cazin, C. S. J.; Slawin, A. M. Z.; Lhermitte, C.; Prabhakar, R.; Germain, M. E.; Palluccio, T.; Nolan, S. P.; Rybak-Akimova, E. V.; Temprado, M.; Captain, B.; Hoff, C. D. *J. Am. Chem. Soc.* **2011**, *133*, 1290–1293.
- (6) Popp, B. V.; Wendlandt, J. E.; Landis, C. R.; Stahl, S. S. *Angew. Chem., Int. Ed.* **2007**, *46*, 601–604.
- (7) Wever, R. In *Vanadium: Biochemical and Molecular Biological Approaches*; Michibata, H., Ed.; Springer: New York, 2012; pp 95–125.
- (8) Conte, V.; Coletti, A.; Floris, B.; Licini, G.; Zonta, C. *Coord. Chem. Rev.* **2011**, *255*, 2165–2177.
- (9) Butler, A.; Clague, M. J.; Meister, G. E. *Chem. Rev.* **1994**, *94*, 625–638.
- (10) (a) Egdal, R. K.; Bond, A. D.; McKenzie, C. J. *Dalton Trans.* **2009**, 3833–3839. (b) Waidmann, C. R.; DiPasquale, A. G.; Mayer, J. M. *Inorg. Chem.* **2010**, *49*, 2383–2391.
- (11) (a) Arzoumanian, H.; Petrianni, J. F.; Pierrot, M.; Ridouane, F.; Sanchez, J. *Inorg. Chem.* **1988**, *27*, 3377–3381. (b) Hagadorn, J. R.;

- Arnold, J. *Inorg. Chem.* **1997**, *36*, 2928–2929. (c) Hanna, T. E.; Lobkovsky, E.; Chirik, P. J. *Inorg. Chem.* **2007**, *46*, 2359–2361. (d) Jeske, P.; Haselhorst, G.; Weyhermüller, T.; Wiegardt, K.; Nuber, B. *Inorg. Chem.* **1994**, *33*, 2462–2471. (e) Lyashenko, G.; Saischek, G.; Pal, A.; Herbst-Irmer, R.; Mösch-Zanetti, N. C. *Chem. Commun.* **2007**, 701–703. (f) Matoga, D.; Szklarzewicz, J.; Mikuriya, M. *Inorg. Chem.* **2006**, *45*, 7100–7104. (g) Matoga, D.; Szklarzewicz, J.; Samotus, A.; Burgess, J.; Fawcett, J.; Russell, D. R. *Polyhedron* **2000**, *19*, 1503–1509. (h) Qin, K.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 2333–2335. (i) Sofetis, A.; Fotopoulou, F.; Raptopoulou, C. P.; Zafropoulos, T. F.; Perlepes, S. P.; Klouras, N. *Polyhedron* **2009**, *28*, 3356–3360. (j) Stanciu, C.; Jones, M. E.; Fanwick, P. E.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 12400–12401. (k) Van Asselt, A.; Trimmer, M. S.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 8254–8255. (l) Yokoyama, A.; Han, J. E.; Cho, J.; Kubo, M.; Ogura, T.; Siegler, M. A.; Karlin, K. D.; Nam, W. *J. Am. Chem. Soc.* **2012**, *134*, 15269–15272.
- (12) (a) Groysman, S.; Goldberg, I.; Goldschmidt, Z.; Kol, M. *Inorg. Chem.* **2005**, *44*, 5073–5080. (b) Liu, Z.; Anson, F. C. *Inorg. Chem.* **2001**, *40*, 1329–1333. (c) Tsuchida, E. *Coord. Chem. Rev.* **2003**, *237*, 213–228.
- (13) Palluccio, T. D.; Rybak-Akimova, E. V.; Cai, X.; Majumdar, S.; Temprado, M.; Silvia, J. S.; Cozzolino, A. F.; Tofan, D.; Cummins, C. C.; Captain, B.; Hoff, C. D. In preparation.
- (14) Tatiarsky, J.; Pacigová, S.; Sivák, M.; Schwendt, P. *J. Argent. Chem. Soc.* **2009**, *97*, 181–198.
- (15) Sergienko, V. S. *Crystallogr. Rep.* **2004**, *49*, 907–929.
- (16) (a) Grzywa, M.; Łasocha, W. Z. *Kristallogr.* **2007**, *222*, 95–98. (b) Won, T.-J.; Barnes, C. L.; Schlemper, E. O.; Thompson, R. C. *Inorg. Chem.* **1995**, *34*, 4499–4503.
- (17) (a) Cambridge Structural Database, version 5.3, Nov 2011 with 586977 entries. (b) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380–388.
- (18) (a) Desiraju, G.; Steiner, T. *The Weak Hydrogen Bond*; Oxford University Press: Oxford, U.K., 1999. (b) Weinhold, F.; Klein, R. A. *Mol. Phys.* **2012**, *110*, 565–579.
- (19) (a) Rybak-Akimova, E. V.; Marek, K.; Masarwa, M.; Busch, D. H. *Inorg. Chim. Acta* **1998**, *270*, 151–161. (b) Fry, H. C.; Scaltrito, D. V.; Karlin, K. D.; Meyer, G. J. *J. Am. Chem. Soc.* **2003**, *125*, 11866–11871.
- (20) Mayer, I. *Int. J. Quantum Chem.* **1984**, *26*, 151–154.
- (21) Glendening, E. D.; Badenhop, J. K.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 628–646.
- (22) Odom, A. L.; Cummins, C. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **1995**, *117*, 6613–6614.
- (23) Yang, W.; Parr, R. G.; Pucci, R. J. *Chem. Phys.* **1984**, *81*, 2862.
- (24) (a) Leung, W.-H.; Chim, J. L. C.; Williams, I. D.; Wong, W.-T. *Inorg. Chem.* **1999**, *38*, 3000–3005. (b) Clough, C. R.; Greco, J. B.; Figueroa, J. S.; Diaconescu, P. L.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **2004**, *126*, 7742–7743. (c) Figueroa, J. S.; Piro, N. A.; Clough, C. R.; Cummins, C. C. *J. Am. Chem. Soc.* **2006**, *128*, 940–950.
- (25) (a) Thomas, S.; Lim, P. J.; Gable, R. W.; Young, C. G. *Inorg. Chem.* **1998**, *37*, 590–593. (b) Nielson, A. J.; Hunt, P. A.; Rickard, C. E. F.; Schwerdtfeger, P. *J. Chem. Soc., Dalton Trans.* **1997**, 3311–3318.
- (26) Brask, J. K.; Fickes, M. G.; Sangtrirutnugul, P.; Durà-Vilà, V.; Odom, A. L.; Cummins, C. C. *Chem. Commun.* **2001**, 1676–1677.